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CHEMICAL SCIENCES

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OTTAWA, CANADA

CANADIAN JOURNAL OF RESEARCH

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NOTICE

The Canadian Journal of Research is at present published in six sections, A to F. Starting with January 1, 1951, these sections will be published as separate journals under distinctive names and the designation Canadian Journal of Research will no longer be used. The present names and the corresponding new names are as follows:

Present Name	*New Name*
Canadian Journal of Research, Section A (Physical Sciences)	Canadian Journal of Physics
Canadian Journal of Research, Section B (Chemical Sciences)	Canadian Journal of Chemistry
Canadian Journal of Research, Section C (Botanical Sciences)	Canadian Journal of Botany
Canadian Journal of Research, Section D (Zoological Sciences)	Canadian Journal of Zoology
Canadian Journal of Research, Section E (Medical Sciences)	Canadian Journal of Medical Sciences
Canadian Journal of Research, Section F (Technological Sciences)	Canadian Journal of Technology

In order to preserve continuity the present sequence of volume numbers will be retained, and in each case the volume for 1951 will be Volume 29.

The subscription rates for the Journals will remain as at present.

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VOL. 28, SEC. B. OCTOBER, 1950 NUMBER 10

AN 80°C. ISOTHERMAL CALORIMETER[1]

BY C. C. COFFIN, J. C. DEVINS,[2] J. R. DINGLE,[3]
J. H. GREENBLATT,[4] T. R. INGRAHAM,[5] AND S. SCHRAGE[6]

Abstract

An 80° isothermal naphthalene calorimeter analogous to the Bunsen ice calorimeter has been constructed and calibrated. The heat to be measured is made to change the solid/liquid ratio of naphthalene at its melting point, and the resulting volume change is determined by the displacement of mercury in a horizontal capillary tube. The naphthalene chamber is surrounded by the vapor of benzene boiling under an automatically controlled pressure at the melting point of naphthalene. The benzene vapor and the partially frozen naphthalene are separated by an evacuated space.

This 80° calorimeter is four times as sensitive as the ice calorimeter and is much more convenient to operate. It is readily adapted to micro work and can be used for fast or slow endothermic or exothermic processes. In the setup described, heats up to about 400 cal. may be measured with a reproducibility of the order of 0.1%. Two different methods of calibration, however, gave "constants" differing by almost 1%. It is thus evident that the instrument must be calibrated as nearly as possible in the way in which it is to be used.

Introduction

The classical example of an instrument making use of the latent heat of fusion as a thermal measure is the Bunsen ice calorimeter (3), an instrument too well known to call for description here. Its advantages and shortcomings are adequately dealt with by Griffiths (8), Swietoslawski (13), and more recently by Ginnings and Corruccini (6). Isothermal calorimeters of a similar type using acetic acid m.p. 16.5°C. (14), diphenylmethane m.p. 24.5°C. (12), diphenyl ether m.p. 26.6°C. (9) and phenol m.p. 40°C. (7, 10, 11) have also been described. With the exception of the ice instrument they have all been operated in automatically controlled liquid thermostats, and do not seem to have been very thoroughly investigated. It seems probable that the potentialities of the method have not been fully explored, particularly in view of the following statement made by White in his authoritative monograph (16). "The ice calorimeter, which dates back to the very beginning of calorimetry, is the most successful of all devices in eliminating thermal leakage, since the

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heat transfer takes place in the interior of a mass of ice whose outer temperature, accurately zero, is the same as that of other ice that surrounds it." The most recent work with the ice calorimeter (6) bears out this statement.

The naphthalene calorimeters described in the present paper resemble the ice calorimeter in that the heat to be measured is made to change the relative amounts of solid and liquid naphthalene at its melting point. The resulting volume change is determined and translated into calories by observing the displacement of mercury in a horizontal capillary tube. The calorimeter proper is insulated by surrounding it with the vapor of benzene boiling under a constant adjustable pressure at the melting point of naphthalene. The partly melted naphthalene and the benzene vapor are separated by a highly evacuated space.

This 80° calorimeter is four times as sensitive as the ice calorimeter (the volume change per added calorie is $+0.00410$ cc. for melting naphthalene as against -0.00104 cc. for melting ice); it can be readily adapted to micro and semimicro work and to exothermic or endothermic processes of short or long duration. It is much more convenient to operate than the ice calorimeter, and the troublesome and erratic "drift" which many experimenters have claimed to be a characteristic of the latter can be almost entirely eliminated for long periods of time by adjusting the pressure on the boiling benzene. This pressure is kept constant at any desired value by means of an automatic regulator that has already been described (5).

Although developed primarily for measuring directly the heats of certain organic reactions that go too slowly at the temperatures of conventional calorimetry, this instrument gives promise of having several other useful applications. It has the same limitations of size and design and therefore in another temperature range has much the same field of usefulness as the ice calorimeter which is particularly well adapted for measuring heats of adsorption, heat capacities, etc. For the study of heats and rates of reaction it is possible to release catalysts and to mix and stir reactants that are already in the calorimeter.

In this calorimeter as operated at present, heats of reaction can be measured with a reproducibility of about 0.2%. This is more than good enough to justify its use in determining the heats of reaction of organic compounds, which can rarely be obtained 100% pure. It must be emphasized that the heats of most organic reactions are as yet known only as the difference between two large numbers—the heats of combustion of products and reactants—and are therefore subject to large errors. To obtain data accurate enough to bring to light any relation between bond energy and molecular structure the heats should in general be measured directly at temperatures high enough for the reaction to go at a convenient rate. Its relatively high operating temperature makes the naphthalene calorimeter suitable for studying both the heats and rates of a variety of liquid phase reactions. The isothermal feature does away

with the necessity of all corrections involving the heat capacities of reactants and products. Because of the absence of metallic leads, most of the thermal leakage corrections involved in ordinary calorimetry are eliminated. Moreover, in contrast with many modern calorimeters of comparable precision, the instrument described here requires no elaborate electrical controls or accessories, which add materially to the cost of the apparatus and to the complexity of its operation.

By using other pairs of substances, one of which boils at about the same temperature as the other melts, it appears possible to develop a series of such isothermal calorimeters covering a wide temperature range and having a variety of applications. For example, preliminary experiments have indicated that with anthracene (m.p. 218.0°C.) and naphthalene (b.p. 217.9°C.) a sensitive calorimeter operating at 218°C. can be constructed. At such a temperature many reactions go rapidly enough to enable their heats to be measured directly. It is hoped also to use this 218°C. calorimeter for a direct determination of the heats of annealing or recrystallization of soft metals, and of the amount of energy stored in a metal by cold-working. A lower temperature combination (benzalacetone, m.p. 40°C. and methylal, b.p. 40°C.), is described in a following paper and gives promise of finding application in studying the heats and rates of certain enzymatic and bacteriological processes (4).

Experimental

Construction of the Calorimeter

Six naphthalene calorimeters of different sizes and designs have been built and tested. The one (No. 6) found to be the most satisfactory is described in detail in the present paper, and is shown diagrammatically in Fig. 1 which has been drawn roughly to scale. Fig. 2 shows the pyrex glass instrument with its outer lagging removed and all the naphthalene melted. The diagram represents the apparatus set up to measure the heat capacity of a specimen, *27*. The tube, *1*, into which the specimen is to be dropped, and which contains oil or mercury to facilitate heat transfer, is surrounded by an annular chamber, *2*, containing highly purified naphthalene at its melting point. On the outside of the inner tube (total depth 35.0 cm., internal diameter 4.0 cm.), and kept from slipping down by a series of glass studs, is a sheath of frozen naphthalene. Volume changes in *2*, due to melting or freezing of the naphthalene by heat changes in *1*, are communicated to the mercury in the bottom of the chamber, and are measured in a calibrated 4 m. horizontal capillary tube connected at *15* and backed by a stainless steel tape graduated in millimeters. The position of the mercury in the capillary can be adjusted by means of the reservoir and tap *13* and *14*. Tube *3* is a vacuum jacket to cut down heat exchange between the naphthalene and the outer chamber, *4*, which contains the vapor of benzene boiling under a constant pressure. When the calorimeter is in operation the outer tube is insulated with a heavy felt jacket, provided with "zipper"

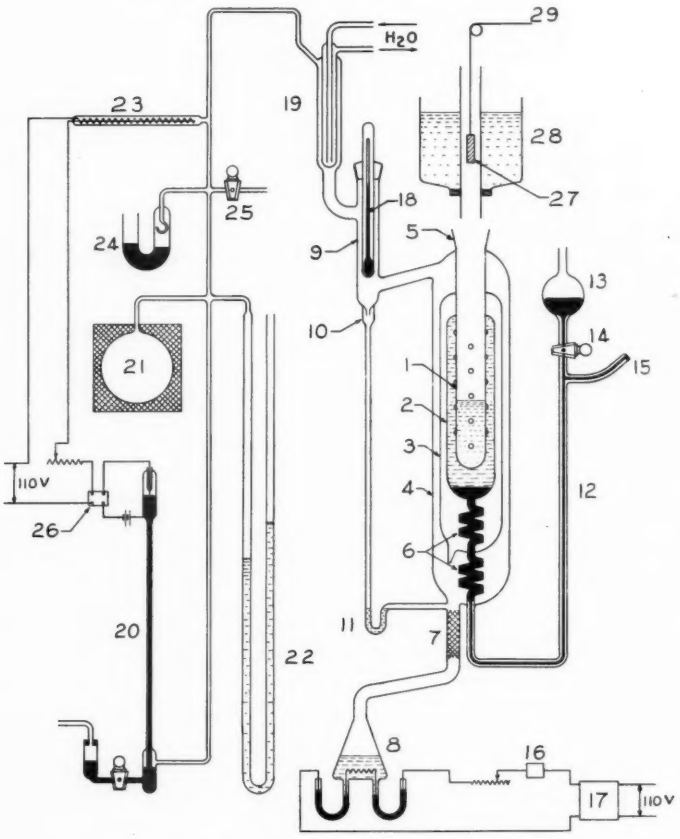

FIG. 1. *Diagram of calorimeter.*

fasteners and lined with aluminum foil to cut down radiation. The spirals *6* are provided to take up expansion inequalities in the apparatus.

The benzene boiler, *8*, containing a nichrome heating coil, is connected to the calorimeter proper through a short packed column, *7*, to prevent superheated vapor reaching the chamber *4*. The vapor is condensed in *19* and returned to the boiler through the drop-counter *10* in a manner obvious from the diagram. All hot tubing between boiler and condenser is heavily insulated with felt or asbestos. To obtain steady boiling during a measurement, the benzene heater must be run off batteries or a constant voltage transformer, *17*.

The upper end of the condenser, *19*, is connected as shown to a manometer *20*, an insulated surge volume *21*, and a tube *23* which contains a nichrome heating coil. If the total pressure in the closed benzene system decreases (e.g., because of a fall in room temperature), the mercury in the manometer

breaks contact with the platinum point sealed through the top, and the electronic relay *26* closes the circuit through the coil in *23*. The pressure in the closed system is thus increased, the relay circuit is closed, and the heater circuit is broken. Tube *23* should be made of brass and be fixed in a horizontal position to facilitate cooling. When the power input in *23* is adjusted until the times of "make" and "break" are about equal, the relay operates every

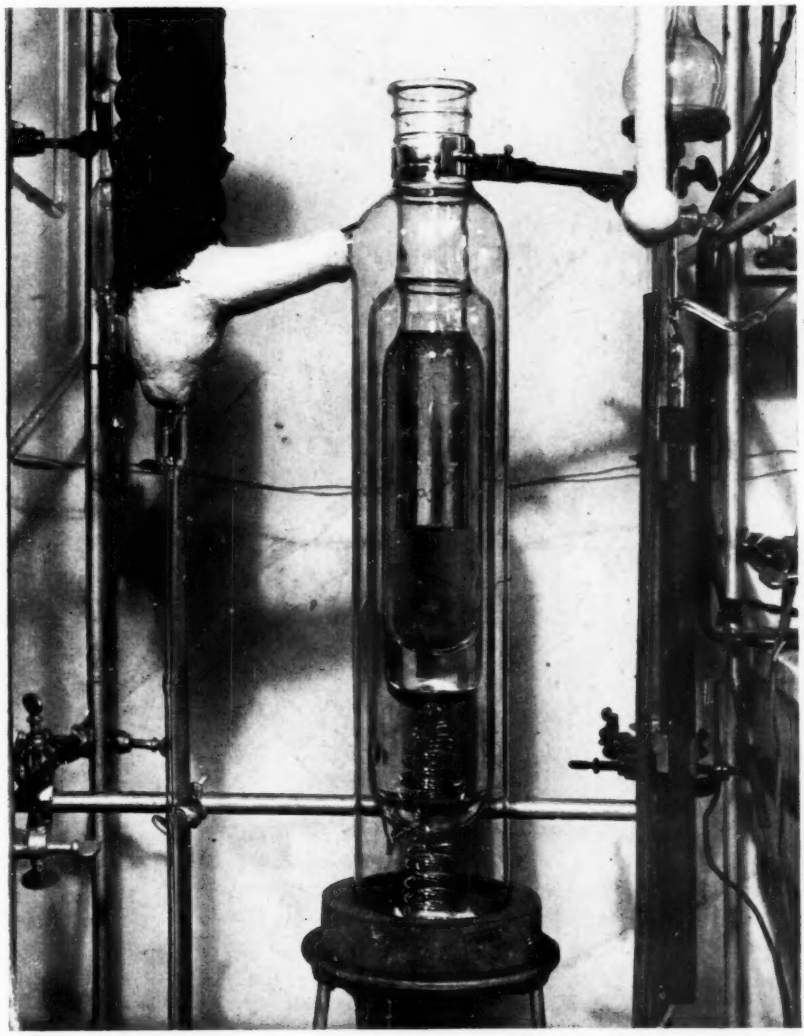

FIG. 2. *Photograph of the calorimeter.*

few seconds and the temperature registered by the Beckmann thermometer *18* remains constant even with large changes in room temperature and atmospheric pressure. When the regulator is properly adjusted, and the volumes of *23* and *21* are in the proper ratio, there is no difficulty in keeping the calorimeter drift constant or practically zero for hours at a time. (A change in room temperature sufficient to affect appreciably the density of the mercury column of the barostat is of course accompanied by a change in calorimeter drift.) The desired pressure, never differing by more than 2 or 3 cm. of mercury from atmospheric, is obtained by adjusting the amount of mercury in the control manometer and the amount of air in the system (tap *25*). The oil manometer, *22*, is convenient in making these adjustments. The mercury filled U-tube, *24*, acts as a two-way safety valve in case the power or water supply is interrupted.

Fig. 3 represents two other calorimeter designs that have proved to be almost as satisfactory for many purposes as that just described, and which are more easily constructed. The numbers in the diagrams correspond to the

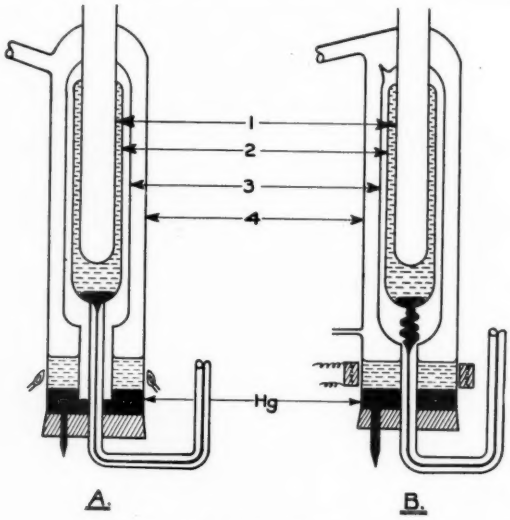

FIG. 3. *Tested types of calorimeter.*

same structural features as in Fig. 1. In each case the lower connection between the outer jacket (which serves as the benzene boiler) and the rest of the assembly consists of a large rubber stopper protected from the boiling benzene by a layer of mercury. In Model A the molten naphthalene and the benzene vapor are separated by an air jacket, the open lower end of which is sealed off from the benzene vapor by dipping into the mercury covering the rubber stopper. In Model B this insulating chamber has been evacuated and sealed off. Model A is heated by small gas jets and B by an external electric heater. All other structural details are essentially the same as those of Fig. 1.

The calorimeters are filled as follows. After cleaning and drying and before sealing on boiler or condenser, a straight length of capillary tubing connecting with chamber *2* through spirals *6* is sealed on to the bottom of the benzene jacket. Chamber *2* is thoroughly evacuated through this tube, which is then sealed off, leaving a fine tip. The whole apparatus is now mounted vertically and this tip is broken off under the surface of purified molten naphthalene floating on a layer of clean mercury so that chamber *2* begins to fill. When sufficient naphthalene has entered, the naphthalene–mercury container is raised so that mercury follows the naphthalene into the chamber. To keep the naphthalene molten during filling, steam is passed through the outer jacket *4*. When chamber *2* is completely filled the steam is turned off and the apparatus is left in an upright position with the capillary under the mercury until the naphthalene has completely solidified. It is then inverted, again evacuated (molten naphthalene dissolves appreciable quantities of air, which is evolved on crystallization) and if necessary more mercury is added through a capillary funnel. The capillary on the calorimeter is now bent to form the U-tube *12* connecting with the measuring capillary, the whole apparatus is returned to the upright position, and the remaining connections (*7*, *11*, *9*) are sealed on.

Operation of the Calorimeter

The operation of these calorimeters can best be described by referring to Fig. 1. For an endothermic measurement, e.g., the heat capacity of a specimen between room temperature and 80°C., a thin uniform mantle is required. This is obtained by melting almost all the solid that may be present and by freezing on a fresh film. Melting is done from the inside by stirring the oil with tubes of hot water, and from the outside by focusing an infrared lamp on the crystals; it is not necessary to change the benzene temperature. Freezing is done by simply stirring the oil for a few seconds with a tube filled with cold water. The quantity of oil and the size of the cold tube should be such that, when the latter is resting on the bottom of tube *1*, the oil level is above the top of the naphthalene chamber. At least a few crystals from a previous mantle must be present to prevent supercooling. If supercooling does occur crystallization can be induced by touching the inner wall with a piece of "dry ice".

If heat evolved is to be measured, a heavier mantle is necessary. A long slender U-tube or cold finger through which water is flowing, and to which an oil-soaked pad of glass wool is attached, is convenient for thickening any desired spot on such a mantle. The progress of freezing may be watched by removing the felt jacket. There must be no holes in the mantle nor any bridges of solid between tubes *1* and *2*. During all mantle adjustments, and indeed all the time that a run is not actually being made, the bent-down far end of the filled measuring capillary is kept immersed in mercury to prevent the possibility of air being sucked back into the naphthalene.

It has been found that better results are obtained, presumably because phase equilibrium is more readily established, if, at the beginning of a run,

there is a thin film of liquid naphthalene between the wall of the calorimeter tube and the solid mantle. In making a series of endothermic measurements, therefore, a tube of hot water is dipped into the oil for an instant before settling the calorimeter for the initial rating period of each run. Before making the first of a series of exothermic runs also, a thin film of liquid should be "flashed" on the outside of the calorimeter well.

After preparing the mantle the felt jacket is replaced, a cotton plug is inserted in the calorimeter neck *5*, the end of the mercury thread is brought (by suction on *13*) to a suitable place on the capillary, and, if necessary, the pressure on the boiling benzene is adjusted until the drift is small. When the drift becomes constant for several consecutive five-minute intervals the run is started by quickly removing the cotton plugs from specimen tube and calorimeter and dropping the specimen from a known temperature. The specimen is allowed to fall freely at the end of its thread until it almost reaches the surface of the oil in the calorimeter. The thread is fixed to stop the fall at this point, so that oil cooled by the specimen will not splash up the inner tube above the top of the naphthalene jacket and thus take heat from the benzene rather than from the naphthalene. As soon as the thread has become taut, the specimen is dropped once more, this time on to a shock-pad of glass-wool at the bottom, and the cotton plug is replaced in the calorimeter opening. In order to provide stirring, the other end of the thread is attached (at *29*) to an already running eccentric of adjustable speed and throw. The thread passes up and down through the center of the cotton plug, which is provided with a slit for the purpose. The plug can be removed, the specimen dropped without splashing, the stirring started, and the plug replaced in about five seconds. Careful alignment is necessary to prevent the specimen from hitting the walls of the calorimeter tube during its fall. The mercury in the measuring capillary starts to move as the specimen enters the oil and, when it begins to slow down (after 5 to 20 min.), its position is read at convenient intervals until its drift has again become constant. The total displacement due to the specimen is determined by extrapolating the fore and after rating periods in the usual way. With highly purified naphthalene the drifts before and after a run are so nearly the same that little error is involved in the extrapolation. Corrections for heats of stirring and plug removal were determined experimentally by each operator. One centimeter of the 4 m. capillary corresponds to approximately 1 gm-cal., so that as much as 400 cal. may be added to or taken from the calorimeter per run. Four to six runs can be made in a normal working day on a single mantle. Under ordinary operating conditions the benzene heater and pressure control are left on all the time so that the only things to do before starting a day's runs are to bring the end of the mercury thread into the capillary and to check on the state of the mantle. The calorimeter pictured in Fig. 2 has run for periods as long as 18 months without a shutdown—often going for weeks without any more attention than an occasional checkup on the power and water supply. No change in the melting point of the naphthalene nor any sign of contamination at the mercury–naphthalene interface has been observed.

Calibration of the Capillary

The measuring capillary was built up from selected 3-ft. lengths of standard pyrex capillary and was calibrated with a short mercury thread. A complete filling of the capillary gave a mean value of 0.05369 gm. of mercury per cm. On this basis the mean length of the short calibrating thread was 3.334 cm. Deviations from this average were measured with a horizontal cathetometer at about 3 cm. intervals along the capillary and a correction curve was constructed by plotting total deviation against scale reading. A weighing method (see Refs. (6) and (8) for example) of accounting for the displaced mercury would undoubtedly be more satisfactory and was in fact used in some of the preliminary experiments. In the work reported here, however, it was desired to keep track of each run throughout its whole course, and to test the suitability of the apparatus for rate measurements, so that the capillary tube method was adopted. If, as is usually the case, a series of measurements can be designed so as to make use of the same part of the capillary, the errors of calibration become negligible.

Purification of the Naphthalene

In the first calorimeters assembled, the drifts before and after a run were found to be different at the same benzene temperature. The removal of heat made the drift become more positive, while the addition of heat made it more negative; i.e., the change was always toward a lower naphthalene melting point with increase in the solid/liquid ratio, and indicated that impurities were concentrating in the liquid phase as the proportion of solid increased. A careful purification of the naphthalene was accordingly undertaken. Twenty kilograms of chemically pure naphthalene were fractionally frozen many times, crystallized three times from purified methanol, and again subjected to many fractional freezings. These operations were performed in enameled or glass vessels sufficiently well insulated to allow about three-quarters of their (unstirred) contents to solidify in 20 hr. A small quantity of metallic mercury was carried along through most of the crystallizations in order to remove impurities with which it might later react in the calorimeter. The final fraction (about 1 kgm.) was distilled in nitrogen just before filling the calorimeters, which have drifts that are completely independent of the solid/liquid ratio. Three certified (two Reichsanstalt, one Bureau of Standards) 0.1°C. mercury thermometers completely immersed in the well of calorimeter No. 6 agreed that the internal temperature at zero drift is 80.34°C. Correction for the fact that the calorimeter is under a mercury pressure of about 2/3 atm. gives a melting point of 80.32°C. This is a temperature 0.02°C. higher than that found by Ward (15) which appears to be the highest previously recorded for the melting point of naphthalene.

Calibration of the Calorimeter

The reproducibility of the calorimeter was tested, and its calibrations were carried out as nearly as possible in the ways in which it was planned to use it. Three different operators made five series of runs which are summarized in

Table I. Both an endothermic (fast) and an exothermic (slow) process were used. The first (Series C1 and C2) consisted in dropping a weighed quantity of copper (a closely wound double helix of No. 14 wire), kept at a known temperature near that of the room, into the oil-filled calorimeter well where it was stirred as already described; in the second (Series E1, E2, and E3) a measured amount of electrical energy was dissipated in a constantan coil immersed in unstirred oil or mercury in the calorimeter well. Certified and calibrated thermometers, standard cells, potentiometers, resistances, etc., were used throughout. The heat contents of the copper specimen were calculated from the data of Bronson, Chisholm, and Dockerty (2). The following are the details and calculations of a representative run of each type. The "defined" calorie (= 4.1833 international joules) is used unless otherwise stated.

Sample Copper Run

Time, min.	Scale reading, cm.	Drift, cm./5 min.	Corrected scale reading, cm.	Remarks
0	360.19	−0.14	360.78	Initial
5	360.08	−0.11	—	rating
10	359.97	−0.11	—	period
15	359.86	−0.11	360.46	Specimen dropped (temp. 22.59°)
50	37.7			12 five-minute periods
55	37.17			
60	36.86	−0.31		
65	36.65	−0.21		
70	36.46	−0.19		
75	36.31	−0.15	33.85	
80	36.19	−0.12	—	
85	36.08	−0.11	—	Final rating period
90	35.93	−0.15	—	
95	35.80	−0.13	—	
100	35.67	−0.13	33.29	

Drift during initial rating period (15 min.) = (360.78 − 360.46)/3 = −0.109 cm./5 min.

Drift during final rating period (25 min.) = (33.85 − 33.29)/5 = −0.112 cm./5 min.

Average drift in five minutes = −0.11 cm.

Correction for drift during run (12 five-minute periods) = 12 × −0.11 = −1.32 cm. Correction for stirring and plug removal = −1.44 cm. (average of several separate determinations). Total correction = −1.32 + (−1.44) = −2.76 cm.

Corrected movement of mercury in capillary = 360.46 − 33.85 − 2.76 = 323.85 cm.

Temperature change of specimen (54.90 gm.) = 80.34° − 22.59° = 57.75°.

Heat transferred (calculated (Ref. 2)) = 294.99 × cal. (20°).

20° calories per mean cm. of scale = 294.99/323.85 = 0.9105.

Defined calories per mean cm. of scale = 0.9097.

Milligrams of mercury per calorie = 53.69/0.9097 = 59.02.

Sample Electrical Run

Time, min.	Scale, cm.	Drift, cm./5 min.	Corrected scale, cm.	Remarks
0	245.93	—	243.35	
5	245.97	+0.04	—	
10	246.01	+0.04	—	*Potentiometer readings*
15	246.03	+0.02	—	*Amps.* (*Stand. res.*) *Volts* (*Cal. coil*)
20	246.07	+0.04	—	
25	246.11	+0.04	243.54	current on (0.1309) (2.5736)
30				0.1310 2.5740
35				0.1310 2.5740
				0.1310 2.5742
46				current off 0.1310 2.5742
55	353.96			
60	354.09	+0.13		
65	354.19	+0.10		
70	354.27	+0.08		
75	354.34	+0.07		
80	354.41	+0.07	355.20	
85	354.47	+0.06	—	
90	354.52	+0.05	—	
95	354.57	+0.05	355.34	

Drift during initial rating period (25 min.) = (243.54 − 243.35)/5 = 0.038 cm./5 min.
Drift during final rating period (15 min.) = (355.34 − 355.20)/5 = 0.047.
Average drift in five minutes = 0.04 cm.
Correction for drift during run (11 five-minute periods) = 0.04 × 11 = +0.44 cm.
Corrected movement of mercury in capillary = 355.20 − 243.54 − 0.44 = 111.22 cm.

E = 2.5740 v.; I = 0.1310 amp.; t = 1260 sec.
Energy input = EIt = 424.8 joules = 101.5 cal.
Calories per mean cm. of scale = 101.5/111.22 = 0.9129.
Milligrams of mercury per calorie = 53.69/0.9129 = 58.82.

The two series of endothermic copper runs (C1 and C2) and the three series of exothermic electrical runs (E1, E2, and E3) are summarized in chronological order in Table I. They were made independently by three different operators over widely spaced time intervals. It is apparent from this table that, while the calorimeter constants of any one series show an average deviation from the mean of the order of 0.1%, the average constants differ by as much as 1%

TABLE I

SUMMARY OF CALIBRATION RUNS

Series	Mean calorimeter constant		Mean deviation, %	Maximum deviation, %	Number of successive runs	Number of runs included in average
	Cal./mean cm.	Mgm. Hg/cal.				
C1	0.9141	58.75	0.05	0.15	49	25
C2	0.9103	58.99	0.07	0.15	46	33
E1	0.9184	58.46	0.08	0.15	10	10
E2	0.9187	58.45	0.17	0.33	12	11
E3	0.9154	58.65	0.14	0.37	27	23

from series to series. This is to be expected since the main object of the operator, especially in the earlier series, was to test the reproducibility of the apparatus, and calibrate it for use in a definite way, rather than to attempt an absolute calibration. More attention was thus paid to keeping heat leaks constant than to their estimation or elimination.

The runs averaged in each series of Table I were selected as follows. From the data of each operator a sequence of runs could be found in which no major changes of apparatus or technique had been made. From this sequence certain runs known, or suspected for good reasons, to be in error were discarded. Toward the end of the work the main reason for dropping a result was the discovery after the run of a hole in the mantle or a bridge of solid across the naphthalene. All first runs on a new mantle were discarded unless the operators "log" stated definitely that "premelting" had been done. The fifth and sixth columns of Table I give respectively the total number of runs in the series and the number used in obtaining the average listed in Columns 2 and 3.

Discussion

Although the calorimeter may be successfully operated without a knowledge of its true constant, it is of interest to discuss some of the more obvious factors contributing to the spread of the observed "constant" and to note where improvements in design and manipulation could be effected.

Since the thermal head between calorimeter and surroundings, the density of the mercury in the barostat, and the volume of the mercury in the capillary are all affected by changes in room temperature, it is obvious that the room temperature should remain fairly constant both during a run and throughout a series of runs. A constant temperature room would thus be of advantage in using this instrument. Because of a southern exposure, vagaries of the heating system, etc., the temperature of the room containing the described calorimeter was very erratic and sometimes changed by as much as 5°C. in an hour. This proved to be very troublesome and led to the discarding of many runs, particularly in the earlier series. It seems likely that a large part of the variation of results within a series is due to these temperature changes.

The problem of closing the calorimeter involves a consideration of the vertical temperature gradients between the well of the calorimeter and the room. The temperature of the well (i) is always about 55°C. above that of the opening; (ii) during endothermic runs is slightly below that of the walls of the benzene vapor jacket above it; (iii) during exothermic runs is slightly above that of the benzene jacket. One of the chief differences between series C1 and C2 is that in the former a 3 cm. long cotton plug was used while in the latter the plug was 12 cm. long and extended from the calorimeter opening to the top of the naphthalene chamber. Assuming loss by radiation to the room to be the same in each case, the longer plug would be expected to diminish convectional heat transfer from the benzene jacket to the calorimeter well,

with the result that more mercury would be sucked back than in a similar run with the shorter plug. This conclusion is in agreement with the observed result that 0.4% more mercury per calorie is moved when the longer plug is used.

In the electrical runs, heat is developed much more slowly than it is removed in the copper runs and the temperature difference between calorimeter well and benzene jacket will be correspondingly smaller. In the exothermic runs, however, the bottom of the air column is warmer than the top, while in the endothermic runs the reverse is the case. This effect might well more than offset the smaller temperature gradient as far as convection is concerned and result in the heat losses being greater in the electrical runs than are the heat gains in the copper runs.

In series E3 the 12 cm. cotton plug used in E1 and E2 was replaced by a standard taper hollow ground-glass stopper (45/50) in which benzene was refluxed with a small internal electric heater. The current and potential leads of the calorimeter coil were introduced through a narrow central tube in the stopper which was connected by way of its condenser to the main benzene system. The calorimeter well was thus almost completely insulated from the room by an 80°C. jacket, and heat losses by radiation through the opening should have been negligible. The fact that in series E3 0.3% more mercury per calorie is pushed out than in E1 and E2 is in agreement with this conclusion. It must be remembered, however, that the method of closing the calorimeter is not the only difference among the runs summarized in Table I. It is quite possible that the effects of different closures are somewhat obscured by a combination of other minor factors, e.g., different operators, electrical setups, heating coils, techniques of mantle formation, etc.

The usual uncertainty regarding the heat developed in the leads and the heat lost through the leads makes difficult a satisfactory comparison of the copper and the electrical runs. It seems likely, however, that in a calorimeter operating at a temperature 50° to 60°C. above that of its environment heat losses will always tend to outweigh heat gains. The amount of mercury moved in the copper runs would thus be larger than it should be and in the electrical runs smaller than it should be, so that the true calorimeter constant might be expected to lie somewhere between the average values obtained for each type of run, i.e., between 58.87 and 58.52 mgm. of mercury per calorie.

The calorimeter constant may be calculated from the volume change on melting and the latent heat of fusion of naphthalene. Block's (1) value for the former, +0.146 cc. per gm., and Ward's (15) value for the latter, 35.09 cal. per gm., give 56.34 mgm. of mercury per calorie. This is 4% lower than the mean value (58.66) of Table I and is in the direction of heat gain by the calorimeter. No convincing explanation of this anomaly can be offered at the present time.

Many experiments have shown that the calorimeter constant is practically independent of the thickness of the mantle and the method of its formation.

The distance between the calorimeter well and the solid–liquid interface has, however, a marked effect on the time required to reach thermal equilibrium. If, in an exothermic run, the solid mantle is separated from the glass well by only a thin film of liquid, equilibrium is established in five or six minutes. If it is a shell of solid separated from the well by a centimeter or more of liquid, from 20 to 30 minutes are required for the calorimeter to settle down after a run. As would be expected the opposite is true for endothermic runs. In this case rapid response requires a sheath of liquid next to the central tube which, for best results, should probably be made of metal rather than of glass and be supplied with some system of metallic heat-distributing vanes. The need for observing the condition of the mantle makes it impracticable to cut down radiation by silvering the vacuum jacket.

Acknowledgment

The authors are indebted to Mr. A. K. Archibald for assistance with some of the preliminary experiments.

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DIMETHYL-2,2′-BIQUINOLYLS[1]

By J. G. Breckenridge

Abstract

Catalytic dehydrogenation of 4-methylquinoline and 6-methylquinoline has been shown to give the corresponding dimethyl-2,2′-biquinolyls. The ultraviolet absorption spectra of the quinolines and biquinolyls have been measured, and the color reaction of the dimethylbiquinolyls with cuprous ion investigated. In all properties examined the dimethylbiquinolyls and biquinolyl behave in a parallel manner.

The preparation of 2,2′-biquinolyl by the catalytic dehydrogenation of quinoline was first carried out by Wibaut *et al.* (8): the product was of interest since it failed to give a color with ferrous iron (the "ferroin" reaction), a situation which is now explicable on the basis of the steric requirements. We have extended the catalytic dehydrogenation reaction to some of the methylquinolines, with the object of comparing the properties of the products with those of the unsubstituted biquinolyl.

The methylquinolines investigated were those with methyl groups in the 4-, 6-, 7-, and 8-positions, and, when the reaction was carried out under essentially the same conditions as used for quinoline, dimethylbiquinolyls were obtained from the 4- and 6-methylquinolines. In the case of quinoline, Wibaut *et al.* (8) reported a yield of 15%; in subsequent work the present author reported (2) a yield of nearly 50%. We have since been unable to repeat this improved yield; many repetitions of the procedure under a variety of experimental conditions have in no case given a yield greater than 20%, and in most cases less than 10%. The reaction both with quinoline and the methylquinolines has been very capricious, experiments carried out under apparently identical conditions having given widely varying yields. An average yield of 30% has been fairly consistently obtained from 4-methylquinoline, but with 6-methylquinoline the yields were extremely low, of the order of 1%, and in many runs no product could be isolated. Repeated experiments with 7- and 8-methylquinolines gave no detectable yield.

It was desirable to investigate the structure of the products, even though it might be reasonably expected that they would have the quinoline rings joined at the 2,2′ positions. In the case of 2,2′-biquinolyl, this proof had been given by the identity of the dehydrogenation product with the compound obtained by a condensation between *o*-aminobenzaldehyde and diacetyl (7). We have attempted to carry out a reaction under similar conditions between *o*-aminoacetophenone and diacetyl, hoping to obtain 4,4′-dimethyl-2,2′-biquinolyl, but no identifiable product could be isolated. However, reaction between 2-chloro-4-methylquinoline and copper powder at 218°C. resulted in a small yield of a

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Contribution from the Department of Chemical Engineering, University of Toronto, Toronto, Ont.

substance which was identical (melting point, mixed melting point) with that obtained by dehydrogenation of 4-methylquinoline, and, in view of other points of comparison dealt with below, it is concluded that the 2,2′ bond joining the rings is common to both the new products.

An obvious means of comparison was the absorption spectra of the compounds involved, and we have measured the ultraviolet absorption spectra (in absolute ethanol) of quinoline, three methylquinolines, the biquinolyls, and a biquinolyl in which the rings are joined at the 8,8′ positions. The results are shown in Figs. 1 and 2.

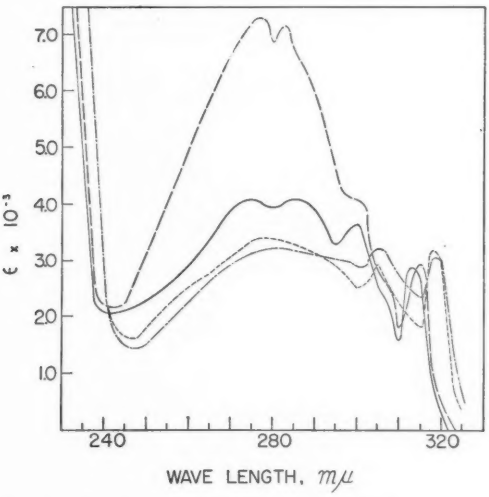

FIG. 1. *Spectra of quinoline and methylquinolines.*
——————— *Quinoline*
— — — — *4-Methylquinoline*
- - - - - - *6-Methylquinoline*
— - — - *7-Methylquinoline*

The ultraviolet absorption spectrum of quinoline has been measured several times, the most recent results being those of Miller *et al.* (4). Our results agree reasonably well with those of Miller (who used 95% ethanol as a solvent), particularly in the position of the two sharp peaks at 313 and 300 mμ, although the values for the molar extinction coefficient differ somewhat. The spectra for the 6- and 7-methylquinolines are very similar in form to that of quinoline, the main differences being shifts of about 5 mμ of the two sharp peaks to longer wave length, and much less clearly defined maxima in the region of 280 mμ. The spectrum of 4-methylquinoline is of the same general form as the others, but has a much higher value of the extinction coefficient in the 280 mμ region, two fairly sharply defined peaks appearing at 283 and 277 mμ. The slight bathochromic shift observed with the 6- and 7-methylquinolines is in line with

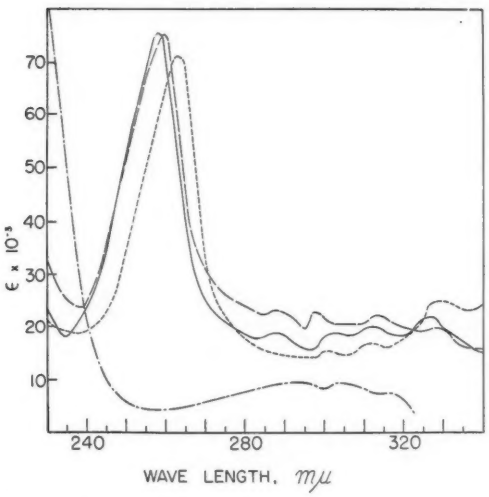

FIG. 2. *Spectra of biquinolyls.*
——————— *2,2'-Biquinolyl*
— — — — *4,4'-Dimethyl-2,2'-biquinolyl*
- - - - - - *6,6'-Dimethyl-2,2'-biquinolyl*
— - — - *8,8'-Biquinolyl*

the general effect of substituent groups in an aromatic system, and that 4-methylquinoline might show some anomalies might have been anticipated from a comparison between its chemical properties and those of quinoline.

The outstanding feature of the spectra of the biquinolyls is the great increase in maximum extinction coefficient. The spectra of 2,2'-biquinolyl and the two new products are very similar, the main peak appearing at 258 mμ for biquinolyl, at 260 mμ for the 4,4'-dimethylbiquinolyl, and at 263 mμ for the 6,6'-dimethyl compound, i.e., slight shifts of the same order as those observed with the quinolines. In addition, the curves between 280 and 330 mμ show a reasonable correspondence: the minor peaks (the height and sharpness of which is obscured by the scale in Fig. 2) occur at the same wave length in many cases. The spectrum of 8,8'-biquinolyl, shown for comparison, is clearly different, the main peak occurring at 230 mμ ($\epsilon \times 10^{-3} = 82.7$).

Another means of comparison is possible since 2,2'-biquinolyl is a sensitive and specific reagent for cuprous ion (2,3). The introduction of methyl groups into the molecule in the 4,4' and 6,6' positions should not affect the steric requirements of the molecule in so far as complex formation is concerned, and should affect only slightly the wave length of maximum absorption and the value of the extinction coefficient, as has been shown for methylphenanthrolines by Brandt and Smith (1). We have found this to be the case, since both dimethylbiquinolyls are almost indistinguishable from 2,2'-biquinolyl in their behavior toward cuprous ion in so far as sensitivity and selectivity are con-

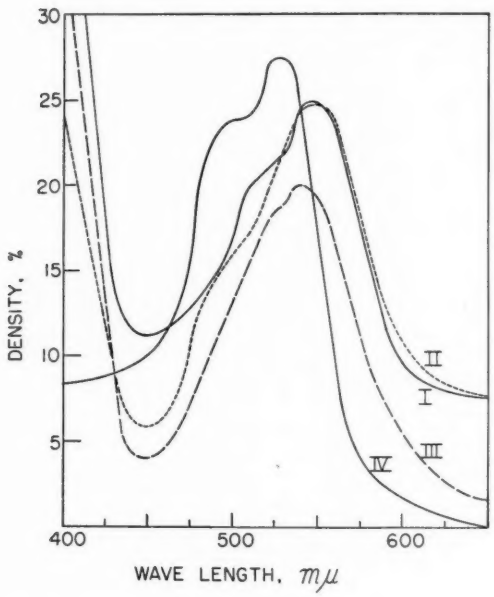

FIG. 3. *Spectra of complexes with cuprous ion.*
I *2,2′-Biquinolyl*
II *4,4′-Dimethyl-2,2′-biquinolyl*
III *6,6′-Dimethyl-2,2′-biquinolyl*
IV *2,2′-Bipyridyl*

cerned, and the absorption spectra of solutions of the cuprous ion complexes are very similar, as is evident from Fig. 3. The spectrum of the complex with 2,2′-bipyridyl is shown for comparison purposes.

The color reaction of 4,4′-dimethylbiquinolyl with cuprous ion was examined further (6), and was found to occur under conditions similar to those for 2,2′-biquinolyl. The complex responsible for the color had a base: metal ratio of 2: 1, was stable over long periods of time, and showed best color development in the pH range 2.3 to 2.7. Beer's law was shown to hold for concentrations of cuprous ion between 1 and 22 p.p.m. The reaction with other ions was tested, and it was found that the reagent was specific for copper under the conditions used, as had been the case with 2,2′-biquinolyl.

Further investigations are in progress on the reactions of 4,4′-dimethylbiquinolyl, taking advantage of the reactivity of the methyl groups, and it has been found in preliminary work that many reactions applicable to 4-methylquinoline which lead to compounds of the cyanine dye type are also applicable to the dimethylbiquinolyl.

Experimental

The quinoline and methylquinolines were synthetic products from the Eastman Kodak Company, and were fractionally distilled before use. The apparatus and procedure used in the dehydrogenation were the same as previously described (2), and the products were recrystallized several times from absolute ethanol. Variations in the reaction temperature of ± 15°C. from the 325°C. previously specified had little effect on the yields, but the rate of shaking of the sealed tubes had to be reasonably vigorous, and the reaction time at least eight hours.

The product from 4-methylquinoline crystallized as small white needles from ethanol or chloroform, m.p. 280° to 281°C.* It could be sublimed *in vacuo* at 240°C. Calc. for $C_{20}H_{16}N_2$: C, 84.5; H, 5.67; N, 9.85%. Found: C, 84.2; H, 5.63; N, 10.1%. The monopicrate was prepared by reaction in benzene solution, and crystallized as orange crystals, m.p. 236°C. (with decomposition). Calc. for $C_{26}H_{19}N_5O_7$: C, 60.8; H, 3.73; N, 13.6%. Found: C, 60.5; H, 3.76; N, 13.5%. The product from 6-methylquinoline crystallized as small white needles, m.p. 259° to 260°C. Found: C, 84.5; H, 5.65; N, 10.2%. The monopicrate, prepared as in the previous case, m.p. 232°C. (with decomposition). Found: C, 60.4; H, 3.70; N, 14.0%. Solutions of both products in ethanol reacted with solutions of copper (II) chloride and cobalt (II) chloride in ethanol to give orange and green crystalline precipitates respectively, indistinguishable in appearance from those obtained before from biquinolyl.

The 8,8'-biquinolyl was prepared from 2,2'-diaminobiphenyl according to the method used by Niementowski and Seifert (5), m.p. 205°C.

A small amount of 4,4'-dimethyl-2,2'-biquinolyl was prepared from 2-chloro-4-methylquinoline in the following manner. Three grams 2-chloro-4-methylquinoline was mixed with copper-bronze and heated in a sealed tube at 218°C. for two hours. The mixture was extracted with ether to remove unreacted starting material, and the residue extracted with hot ethanol. The flocculent precipitate which came down on cooling was treated with ammonia and the residue extracted with chloroform. Evaporation of the chloroform gave a small amount of crystalline product, which was recrystallized twice from benzene. The yield was about 5 mgm., m.p. 280° to 281°C. A mixed melting point with the material from the dehydrogenation reaction showed no depression, and a solution in ethanol gave the characteristic purple color with cuprous ion. Attempts to obtain a better yield by use of the 2-bromo or 2-iodo derivatives failed.

For the work on the ultraviolet absorption spectra, absolute ethanol solutions of the compounds were examined in a Beckman Model DU spectrophotometer, measurements being taken at 2.5 mμ intervals at maximum sensitivity. The concentrations of the solutions used were approximately 0.00015 molar for the

**All melting-points corrected against known standards.*

quinoline and methylquinolines, and 0.00001 molar for the biquinolyls. Silica cells of thickness 1.000 ± 0.004 cm. were used. All readings in the neighborhood of maxima and minima were checked twice.

The absorption spectra in the visible region of the complexes with cuprous ion were also determined on the Beckman spectrophotometer, readings being taken at 5 mμ intervals. The concentrations used were approximately 0.0003 molar.

Acknowledgment

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CHANGES OF DENSITY OF HYDROGEN PEROXIDE SOLUTIONS ON COOLING AND FREEZING[1]

By Paul A. Giguère and Pierre Geoffrion

Abstract

The densities of binary solutions of hydrogen peroxide and water from 0°C. down to their respective freezing point were measured by the dilatometric method with an estimated precision of ± 0.0003 gm. per ml. Volume changes during solidification were also measured but with lower precision. Solutions containing less than about 50% by weight of hydrogen peroxide expand on freezing whereas more concentrated solutions contract appreciably. Various observations on the phenomenon of supercooling seem to indicate that no solid solutions are formed between the two components. Under certain conditions hydrogen peroxide solutions decompose on melting.

The purpose of this investigation was to ascertain what volume changes take place when hydrogen peroxide solutions of various concentrations are cooled and frozen. The problem is of some practical importance now that hydrogen peroxide is manufactured and shipped in highly concentrated form. In addition useful information could be expected on such related questions as supercooling and formation of solid solutions. At first this work was to include measurements of density above 0°C. in order to check the data of Maass and Hatcher (5). However, with the recent publication of the results of Huckaba and Keyes (3) this became unnecessary.

Experimental

The dilatometric method was selected as the most suitable, since it allows measurement of large volume changes and is well adapted to low temperature work. The dilatometers were made by blowing a 4–5 ml. bulb at the end of a 12–15 cm. Pyrex "Tru-Bore" capillary tubing having a 2.5 ± 0.001 mm. internal diameter. Considerable care was taken to render the glass surface inactive by following scrupulously the recommendations of Huckaba and Keyes (3). This phase of the operations proved to be most difficult and frustrating; actually much more time and energy was spent on it than on the density measurements proper.

The distance between the meniscus and the nearest one of three fine grooves etched on the dilatometer stem were measured to ± 0.005 cm. by means of a Gaertner cathetometer. The volume of the bulb and that of the capillary, centimeter by centimeter, were determined with an accuracy greater than one part in 10,000, using freshly distilled water at 25°C. Corrections for the contraction of the bulb at lower temperatures were computed by means of the coefficient of cubical expansion of Pyrex glass; the linear expansion of the capillary stem was entirely negligible.

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Contribution from the Department of Chemistry, Laval University, Québec, Que.

The dilatometers were filled by suction with the device shown in Fig. 1. The solutions were prepared by evaporation under reduced pressure of Becco's 90% hydrogen peroxide appropriately diluted and redistilled twice. The solution was received directly in the 50 ml. flask (shown in Fig. 1) on which the adapter could be fitted. This avoided possible contamination of the liquid on transferring, and reduced the danger of decomposition. Furthermore, the solutions were never allowed to warm above 0°C. from the moment they were condensed in the still until after the density measurements. Weighing of the filled dilatometer was done only at the end of a determination. The analysis of the solutions was by titration with potassium permanganate after the method recommended by Huckaba and Keyes (2).

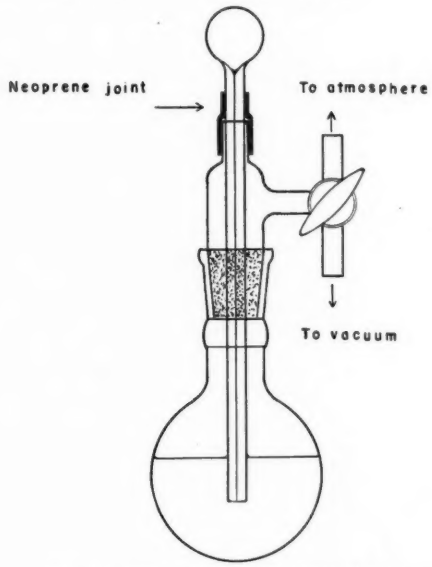

FIG. 1. *Filling device for the dilatometers.*

Once filled, the dilatometer was immediately transferred to a well stirred ice bath where it was left for at least 30 min. before the volume of liquid was measured. Then it was placed in a special bath, Fig. 2, the temperature of which could be adjusted anywhere between 0° and −60°C. and kept constant to 0.1°. The bath proper consisted of a tall Dewar flask *A*, 8 cm. in diameter, filled with methanol. An helicoidal type of stirrer *C* was found to be the most efficient in maintaining adequate circulation in such a tall and narrow vessel. A second Dewar flask *B*, of much larger capacity than *A*, provided the cold head; it too was filled with methanol to which lumps of dry ice were added through a hole in the transite cover *D*. The perforated brass plate *E* prevented the dry ice from sinking to the bottom where it would eventually cause violent foaming. An immersion pump *F*, made entirely of brass and driven by a small

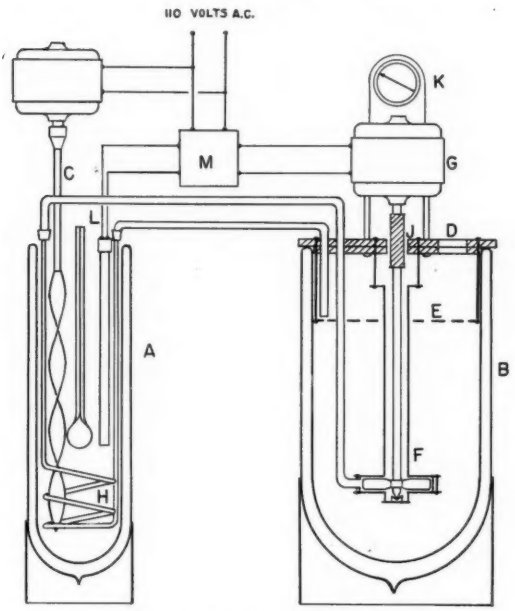

FIG. 2. *Low temperature bath.*

electric motor *G*, provided intermittent circulation of the cold methanol through a copper tubing coil *H* immersed in *A*. The motor was thermally insulated from the pump shaft through a fiber bushing *J*. The system was completed by a rheostat *K* to adjust the speed of the motor, a thermoregulator *L* of the electric resistance type and an electronic relay *M* (Edison, Model 191). For efficient and economical operation a temperature gradient of 10° between the two baths was necessary. The whole unit could be brought to −50°C. and kept at that temperature for eight hours with about 10 lb. of dry ice. The temperature of the small bath was read to 0.1° on a thallium amalgam thermometer.

During a determination the temperature of the bath was gradually lowered in steps and the volume of the liquid measured once the meniscus had come to equilibrium. This usually required 15–20 min. when only liquid was present; after solidification had begun, however, it took much longer. To initiate crystallization, which was seldom spontaneous, the dilatometer had to be brought in contact with dry ice or even liquid air in some cases.

Discussion of Results

Density of Liquid Solutions

Because of difficulties due mostly to catalytic decomposition of hydrogen peroxide only about one third of the more than 30 determinations carried out

could be completed successfully. The results of measurements at 0°C. are given in Table I in grams per milliliter since the dilatometers were calibrated using the value $d_4^{25^\circ} = 0.99708$ for water. Extrapolation leads to 1.4730 gm. per ml. for the density of pure hydrogen peroxide at 0°. When plotted on a large graph the present data agree to within 0.1% on the average with those of Huckaba and Keyes (3). The results of these authors are therefore substantiated in opposition to the lower ones of Maass and Hatcher (5) and of Kubaschewski and Weber (4).

TABLE I

DENSITY OF HYDROGEN PEROXIDE SOLUTIONS AT 0°C.

% H_2O_2 by weight	This work, gm./ml. ± 0.0003	Huckaba and Keyes,* gm./cc. ± 0.0001	% discrepancy
9.3_2	1.0377	1.0366	0.11
10.2_1	1.0410	1.0402	0.08
12.2_1	1.0493	1.0484	0.09
18.3_2	1.0748	1.0735	0.12
19.2_7	1.0783	1.0774	0.08
29.5_4	1.1209	1.1206	0.03
41.2_3	1.1722	1.1715	0.06
49.8_7	1.2119	1.2104	0.12
68.3_7	1.3006	1.2990	0.12
69.0_5	1.3037	1.3024	0.10
78.6_1	1.3535	1.3515	0.15
79.6_3	1.3590	1.3569	0.15
89.6_4	1.4136	1.4116	0.14

**Interpolated from the graph.*

The mean coefficients of cubical expansion

$$\alpha = \frac{V_o - V_t}{V_o \, \Delta t}$$

are listed in Table II along with the temperature intervals over which they were obtained. By extrapolation the expansion coefficient of pure liquid hydrogen peroxide is found to be 7.9×10^{-4} around its freezing point.

TABLE II

MEAN COEFFICIENT OF CUBICAL EXPANSION OF HYDROGEN PEROXIDE SOLUTIONS BELOW 0°C.

% H_2O_2 by weight	Δt	$\alpha \times 10_4$
10.2_1	8.1	1.3 ± 0.5
19.2_7	14.9	3.2 ± 0.3
29.5_4	20.0	4.6 ± 0.2
41.2_3	50.0	5.54 ± 0.09
46.7_2	50.0	5.81 ± 0.09
49.8_7	50.0	6.03 ± 0.11
68.3_7	35.0	6.7 ± 0.1
78.6_1	25.0	7.1 ± 0.2
89.6_4	10.0	7.5 ± 0.4

Volume Changes on Freezing

The curves in Figs. 3, 4, and 5 illustrate the changes of specific volume as a function of temperature. They show readily that whereas the results for the liquid solutions (straight portion of the curves) are quite regular and consistent, the behaviour of the system during crystallization is often erratic. For instance the $19.2_7\%$ solution should exhibit an expansion intermediate between those of the $10.2_1\%$ and the $29.5_4\%$ solutions. Similarly the $46.7_2\%$ solution is abnormal compared to $41.2_3\%$. This is no doubt due to segregation, imperfections in the crystals formed and, possibly, some slight decomposition of the peroxide. Qualitatively it may be said that solutions containing less than 45% by weight of hydrogen peroxide expand on freezing, this effect decreasing with increasing concentration. The reverse is true of solutions over 65% in concentration. No definite conclusion could be reached regarding the relative density of the molecular compound, $H_2O_2.2H_2O$, because of the difficulty of exact measurements at the low temperatures involved.

Depending on their concentration the solutions behave quite differently on freezing. Thus in dilute solutions (less than 45%) crystallization is easily initiated if not spontaneous. The first crystals appear on the walls of the container in the form of tiny white flakes that grow quickly by branching somewhat like hoarfrost. On the other hand, solutions containing over 65% of hydrogen peroxide show marked supercooling, and solidify only slowly owing to their great viscosity. They form clear, long needles growing up in bundle from a nucleus at the bottom of the liquid.

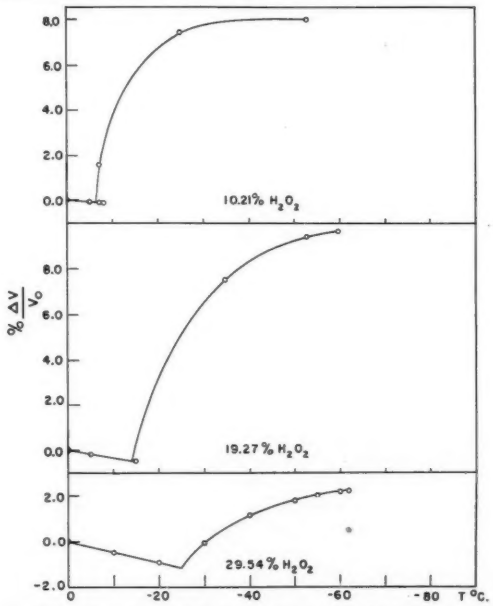

FIG. 3. *Changes of specific volume of hydrogen peroxide solutions on cooling and freezing.*

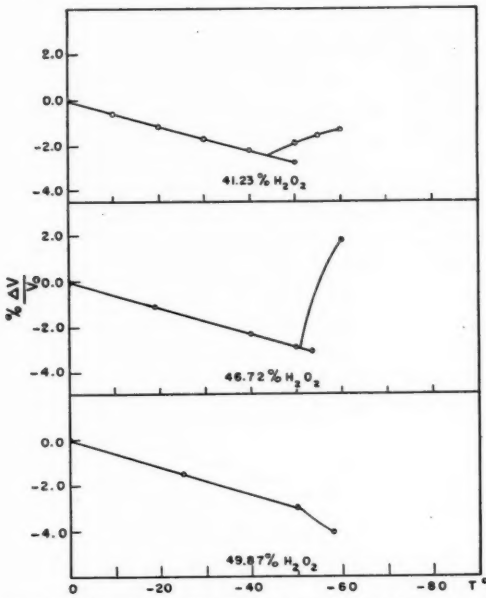

FIG. 4. *Changes of specific volume of hydrogen peroxide solutions on cooling and freezing.*

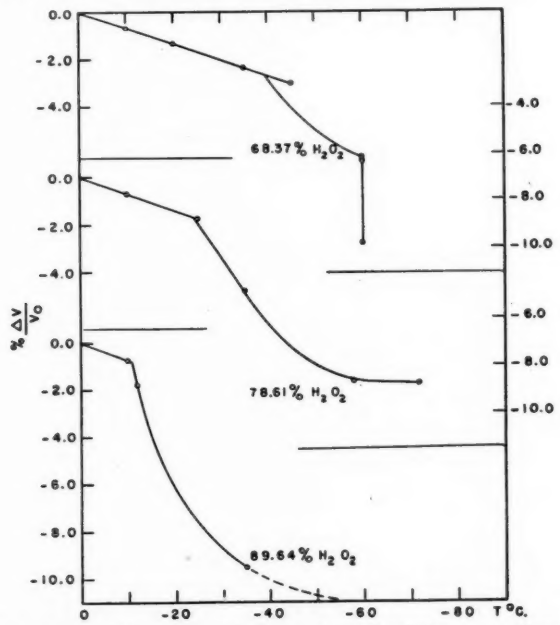

FIG. 5. *Changes of specific volume of hydrogen peroxide solutions on cooling and freezing.*

Supercooling and Solid Solutions

Early experiments had indicated clearly that hydrogen peroxide solutions usually remain partly liquid even at temperatures below their corresponding eutectic, *B* or *D* (Fig. 6). This is especially noticeable in the concentration range 40–65%. In order to check this point further the following test was made. A 41.8% solution placed in a centrifuge tube (for easier separation of the phases) was cooled to about one degree below its freezing point, −46°C. After initiating crystallization by means of dry ice the temperature was lowered slowly to −60°C. and the liquid portion was then siphoned carefully into another test tube at the same temperature. On analysis by means of refractive index the concentration of this mother liquor was found to be 48.4%, whereas that of the eutectic is known to be only about 45% (6). Addition of ice crystals to this liquid produced no noticeable change, but a trace of a crystal from a 45% solution completely frozen in liquid air caused immediate solidification of the whole mass.

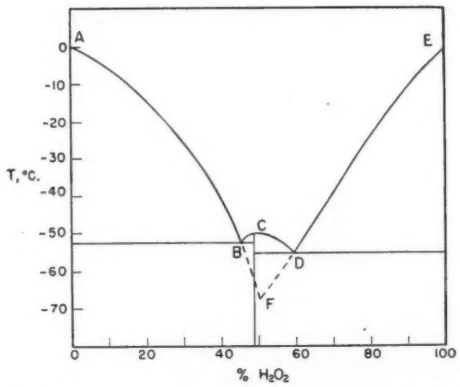

FIG. 6. *Freezing-point curve for the system hydrogen peroxide – water after Maass and Herzberg (6).*

Therefore the system was supercooled with respect to the addition compound, $H_2O_2.2H_2O$, as shown by the dotted line *BFD*. This is considered as an indication that the crystals which separated first along *AB* were pure ice, and not a solid solution as previously reported (1). Indeed, it is conceivable that ice crystals will not initiate separation of the addition compound $H_2O_2.2H_2O$, since water and hydrogen peroxide crystallize in such different systems (hexagonal *vs.* tetragonal). On the other hand, solid solutions would have crystal structures intermediate between those of the two pure compounds and thus should bring about separation of the eutectic mixtures.

As an additional check the specific volumes of partly solidified solutions were calculated by the tie-line method using the density of ice and of solid hydrogen peroxide (5) and the present data for the liquid solutions at corre-

sponding temperatures. As may be seen from Table III the agreement with the experimental values is most always very good in spite of the numerous causes of error. Admittedly this latter argument does not carry much weight, however, since the physical properties of solid solutions are known to vary regularly with concentration between those of the pure components. At any rate this question of solid solutions will be reinvestigated thoroughly in this laboratory.

TABLE III

SPECIFIC VOLUMES OF PARTLY FROZEN SOLUTIONS OF HYDROGEN PEROXIDE

H_2O_2, weight %	T ± 0.1°, C.	Specific volume		Deviation, %
		Calculated	Measured	
10.2$_1$	−25.0	1.015	1.031	1.6
"	−53.0	1.021	1.037	1.5
19.2$_7$	−14.9	0.926	0.925	−0.1
"	−29.8	0.957	0.997	4.0
29.5$_4$	−50.0	0.906	0.908	0.2
41.2$_3$	−50.0	0.835	0.837	0.2
68.3$_7$	−60.0	0.727	0.722	−0.7
78.6$_1$	−35.0	0.708	0.703	−0.7
89.6$_4$	−12.0	0.696	0.694	−0.3
"	−35.0	0.657	0.633	−3.6

Decomposition on Melting

Most attempts to reproduce volume measurements on warming up were useless once the solution had been frozen, because of considerable decomposition of hydrogen peroxide on melting. The same phenomenon has been observed by other investigators while trying to degas samples of peroxide by alternate freezing and thawing (2). A remarkable feature is the fact that the gas bubbles are formed only while the crystals are in the process of melting. Numerous tests have shown that partly frozen mixtures can be kept indefinitely at constant temperature without any sign of decomposition. On the other hand, when a decomposing mixture is cooled further the gas evolution ceases promptly as soon as the thawing stops. That the evolved oxygen results from the decomposition of hydrogen peroxide and is not due to supersaturation of the liquid is proved by this and other observations: The phenomenon appears unchanged whether the solutions are freshly distilled or have been standing at room temperature for some time. In one instance a 99.6% solution was distilled by evaporation under reduced pressure (2–3 mm. mercury) into a receiver cooled in dry ice. On melting, while still under vacuum, the solid produced a marked evolution of gas, which stopped abruptly as the last crystal disappeared. In another test, some crystals obtained by freezing completely a 52% solution were dropped into distilled water where they sank and melted promptly, leaving behind them a trail of minute gas bubbles.

Repeated tests have proved quite conclusively that only the eutectic mixtures are capable of bringing about this decomposition. The first crop of

crystals obtained on slowly freezing the liquid, whether it be the prisms formed in dilute solutions or the long needles in the more concentrated ones, do not promote decomposition on melting. If, however, these original crystals are cooled to low enough temperatures, around −70°C., and kept there for some time, a gradual transformation takes place as evidenced by sharp clicks and a progressive contraction of the mass, which assumes then the appearance of finely fritted glass or compressed snow and becomes detached from the walls of the container. On melting this snowy mass is found to consist of minute needles, less than 1 mm. long, and oriented at random. Under magnification the gas bubbles may be seen to appear in the liquid at the tip of these microcrystals. Solutions in the concentration range 40–65% yield almost exclusively either one of the two eutectic mixtures on freezing; then, on melting, they always decompose with great effervescence.

Explanation of the above phenomenon may rest in the particular nature of the addition compound $H_2O_2.2H_2O$, always present in the eutectic mixtures. In order to fit into the crystal structure of this hydrate the configuration of the hydrogen peroxide molecule must be distorted appreciably, the resulting strain being sufficient to cause dissociation. It may also be a simple case of catalytic decomposition at the surface of microcrystals.

Acknowledgement

The authors wish to acknowledge gratefully the financial assistance received from the Buffalo Electro-Chemical Co. for this project.

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Résumé

Au moyen d'un dilatomètre l'on a étudié les variations de volume, lors du refroidissement et de la congélation, des solutions de peroxyde d'hydrogène de diverses concentrations. La densité de ces solutions à 0°C. a été mesurée avec une précision de l'ordre de 0.0003 g/ml. Les changements de volume pendant la solidification n'ont pu être mesurés avec une précision semblable à cause de difficultés expérimentales et autres. Toutefois l'on peut dire de façon générale que les solutions à moins d'environ 50% en poids augmentent de volume en se congelant, tandis que les solutions plus concentrées se contractent de façon normale. L'examen du phénomène de surfusion semble indiquer que l'eau et le peroxyde d'hydrogène ne forment pas de solutions solides, contrairement à ce qui a été rapporté précédemment. Enfin l'on a observé que les mélanges eutectiques formés aux basses températures catalysent la décomposition du peroxyde d'hydrogène lors de la fusion.

EFFECTS OF POSITION ISOMERISM ON THE PHYSICAL PROPERTIES OF GLYCOLS[1]

By K. A. Clendenning, F. J. Macdonald,[2] and D. E. Wright

Abstract

Specific gravity, refractivity, viscosity, boiling point, and freezing point data are provided for 1,2-propanediol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,2-pentanediol and 1,5-pentanediol, in the pure state and in aqueous solution. The observed molar refraction values agreed closely with M_r values calculated according to Swientoslawski. Lengthening the distance between the hydroxyl substituents increases the specific gravity, refractivity, boiling point, and viscosity, and reduces thermal expansion and isothermal contraction on mixing with water. The order of decreasing effectiveness as freezing point depressants on a weight basis is 1,2-propanediol, *levo*- 2,3-butanediol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,2-butanediol, 1,5-pentanediol, and 1,2-pentanediol. Aqueous solutions of all of these glycols exhibit pronounced specific gravity maxima. The glycol concentration at which maximum specific gravity is attained increases with increasing distance between the hydroxyl substituents.

Introduction

The effects of stereoisomerism on the physical properties of 2,3-butanediols have been treated in earlier papers (3, 4, 11, 13). The present study of propanediols, butanediols, and pentanediols has revealed several consistent effects of position isomerism on the physical properties of aliphatic glycols. The literature reveals that this topic has not previously been subjected to systematic investigation.

Materials and Methods

1,2-Butanediol was synthesized by the acid hydrolysis of butadiene monoxide to 3-butene-1,2-diol followed by reduction of the double bond with hydrogen to yield 1,2-butanediol. Butadiene monoxide* was stirred vigorously in four volumes of water, in the presence of small amounts of hydroquinone and phosphoric acid. When solution was complete, a slight excess of sodium bicarbonate was added and the solution was distilled in vacuum. The 3-butene-1, 2-diol showed boiling points of 89°–92°C. at 3 mm. of mercury and 95°–97°C. at 11 mm. of mercury. Reduction at the double bond was then effected by high pressure catalytic hydrogenation over Raney nickel.

1,4-Butanediol was synthesized by high pressure catalytic hydrogenation of diethyl succinate, according to the method of Adkins and Folkers (1). A large sample of 1,4-butanediol was also obtained through the courtesy of

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Contribution from the Division of Applied Biology, National Research Laboratories, Ottawa. Issued as paper No. 88 on the Industrial Utilization of Wastes and Surpluses and as N.R.C. No. 2221.
[2] *Formerly Biochemist, Industrial Utilization Investigations. Present address: Canadian Industries Ltd., Montreal, P.Q.*
* *Obtained from Columbia Chemical Division, Pittsburgh Plate Glass Company.*

Dr. W. Reppe, I. G. Farben, Ludwigshafen, Germany. 1,3-Butanediol was provided by the Shawinigan Chemicals Corporation, Shawinigan Falls, P.Q. 1,2- and 1,5-Pentanediols, obtained as by-products in the manufacture of tetrahydrofurfuryl alcohol (16), were provided by Dr. L. E. Schniepp of the Northern Regional Research Laboratory, Peoria, Ill. 1,2- and 1,3-Propanediols were obtained from the Eastman Research Laboratory, Rochester, N.Y.

The seven glycols were purified by fractionation at reduced pressure in an 18 in. Stedman column. The glycols were first mildly acidified with dilute oxalic acid solution and distilled *in vacuo*. The neutral fraction collected at constant boiling point and refractive index was then fractionated *in vacuo* over sodium hydroxide pellets. The glycol solutions were made up on an analytical balance, with minimum exposure to air. Specific gravity, isothermal contraction on mixing, thermal expansion, refractivity, viscosity, boiling point, and freezing point were determined by the same methods as were used in corresponding studies of 2,3-butanediol stereoisomers (3, 4).

TABLE I

OBSERVED AND CALCULATED MOLAR REFRACTION DATA FOR PURE GLYCOLS

	Calculated M_r		Observed M_r	
			20°C.	40°C.
1,2-Propanediol	Bruhl	18.95	19.06	19.06
	Eisenlohr (7)	19.10		
	Swientoslawski (18)	18.99		
1,3-Propanediol	Bruhl	18.95	19.04	19.02
	Eisenlohr (7)	19.10		
	Swientoslawski (18)	18.99		
1,2-Butanediol	Bruhl	23.56	23.58	23.63
	Eisenlohr (7)	23.82		
	Swientoslawski (18)	23.61		
1,3-Butanediol	Bruhl	23.56	23.61	23.65
	Eisenlohr (7)	23.82		
	Swientoslawski (18)	23.61		
1,4-Butanediol	Bruhl	23.56	23.60	23.63
	Eisenlohr (7)	23.82		
	Swientoslawski (18)	23.61		
levo-2,3-Butanediol	Bruhl	23.56	23.62 (25°C.)	
	Eisenlohr (7)	23.82		
	Swientoslawski (18)	23.61		
meso-2,3-Butanediol	Bruhl	23.56	23.59 (25°C.)	
	Eisenlohr (7)	23.82		
	Swientoslawski (18)	23.61		
1,2-Pentanediol	Bruhl	28.16	28.18	28.22
	Eisenlohr (7)	28.34		
	Swientoslawski (18)	28.23		
1,5-Pentanediol	Bruhl	28.16	28.23	28.23
	Eisenlohr (7)	28.34		
	Swientoslawski (18)	28.23		

Results and Discussion

The observed molar refractions $(M_r)_D$ are reported in Table I together with M_r values calculated from the atomic refraction constants reported by Bruhl,† Eisenlohr (7), and Swientoslawski (18). Agreement between the observed and calculated M_r values was best when Swientoslawski's constants were employed and was poorest when Eisenlohr's constants were employed. The theoretical M_r values for 2,3-butanediols which were used by Neish (13) and Clendenning (3) were based on Bruhl's constants.† Table I shows that the observed and calculated M_r values for 2,3-butanediols are in better agreement when Swientoslawski's constants are employed. Although Eisenlohr's constants (7) have been indicated to be in error by later investigators (18, 19), they nevertheless were selected for inclusion in the most recent editions of Getman and Daniels' Outline of Physical Chemistry (6, 8) and Remick's "Electronic Interpretations of Organic Chemistry" (15).

Table II reports refractive index, specific gravity, and boiling point measurements on the seven glycols. Our measurements, with one exception, agree

TABLE II

REFRACTIVE INDEX, SPECIFIC GRAVITY, AND BOILING POINT MEASUREMENTS ON PROPANEDIOLS, BUTANEDIOLS, AND PENTANEDIOLS

Compound	Refractive index	Specific gravity, d^{t}_{4}	Boiling point, °C., 760 mm.
1,2-Propanediol	25°C. 1.4316 (17) 1.4313*	23°C. 1.0354 (17)	187 (17)
	20°C. 1.4331 (14) 1.4324*	20°C. 1.0364 (14) 1.0361*	186*
1,3-Propanediol	25°C. 1.4385 (17) 1.4380*	20°C. 1.0538 (17) 1.0529*	215 (17)
	21°C. 1.4394 (17) 20°C. 1.4389*		213.5*
1,2-Butanediol	20°C. 1.4378*	20°C. 1.0024*	190.5*
1,3-Butanediol	25°C. 1.4410 (17) 1.4391 (12) 1.4388*	20°C. 1.0053 (17) 1.0035 (12) 1.002 (2)	207.5 (17) 208 (2)
	20°C. 1.4404 (2) 1.4398*	1.0037*	207*
1,4-Butanediol	20°C. 1.4467 (10) 1.4459 (2) 1.4460*	20°C. 1.0171 (10) 1.0160 (2) 1.0185*	230 (2) 228*
1,2-Pentanediol	24°C. 1.4390 (16) 25°C. 1.4380*	24°C. 0.9691 (16)	210 (16)
	20°C. 1.4390*	20°C. 0.9723*	206*
1,5-Pentanediol	26°C. 1.4480 (16) 25°C. 1.4484*	26°C. 0.9890 (16)	239 (16)
	20°C. 1.4500*	20°C. 0.9914*	238*

*Authors' observations.

†As cited in the fifth and earlier editions of Getman and Daniels' "Outlines of Physical Chemistry," John Wiley and Sons Inc., New York. 1931.

closely with values taken from recent publications. There is a considerable discrepancy in the refractivity and density values for 1,3-butanediol, our values being in closer agreement with those of Michael and Hopkins (12) and Bourns and Nicholls (2) than with those of Shierholtz and Staples (17).

The specific gravity of aqueous propanediol, butanediol, and pentanediol solutions at 20° and 40°C. is shown in Figs. 1–7. The specific gravity of aqueous solutions of these seven glycols, as well as of *meso-* and *levo*-2,3-butanediol (3) attain maximum values that are considerably above that of either the pure glycol or of water. Ethylene glycol as well as simple monohydric alcohols do not have this property. A maximum in specific gravity however is attained in aqueous tetrahydrofurfuryl alcohol solutions (5).

Figs. 1–7 show that the glycol concentration at which this maximum in specific gravity is attained varies in a systematic way with the distance between the hydroxyl substituents; as the hydroxyl groups become more widely separated, the glycol concentration at which the density maximum is attained is progressively increased. This effect is quite apparent in the propanediols and butanediols, but is most strongly expressed in the pentanediols.

The specific gravity and boiling points of the pure glycol isomers also increase with increasing distance between the hydroxyl substituents (Table II, Figs. 1–7). Among the butanediols, the 2,3-isomers show specific gravity and refractive index values which are closer to those of the 1,2- than to those of the 1,3- and 1,4-butanediols.

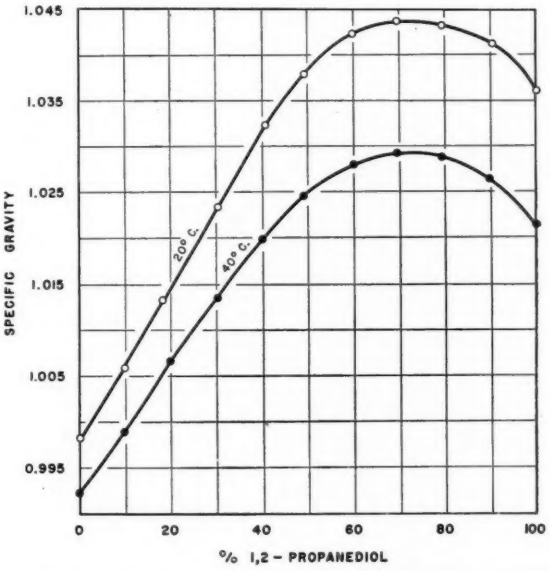

FIG. 1. *Specific gravity of aqueous 1,2-propanediol solutions at 20° and 40°C.*

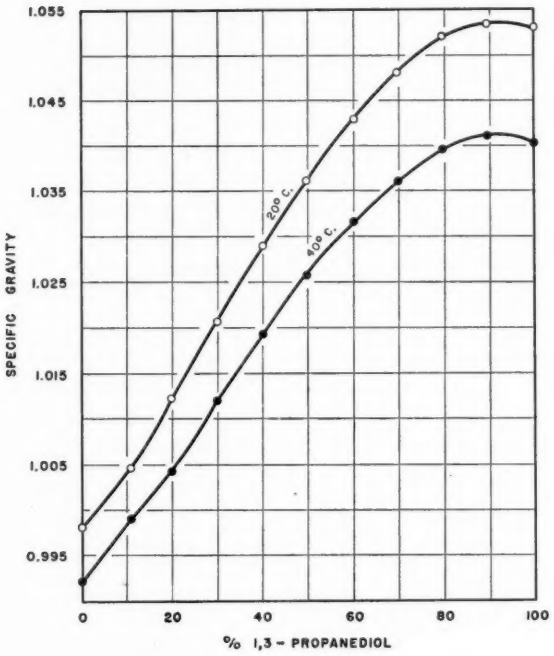

FIG. 2. *Specific gravity of aqueous 1,3-propanediol solutions at 20° and 40°C.*

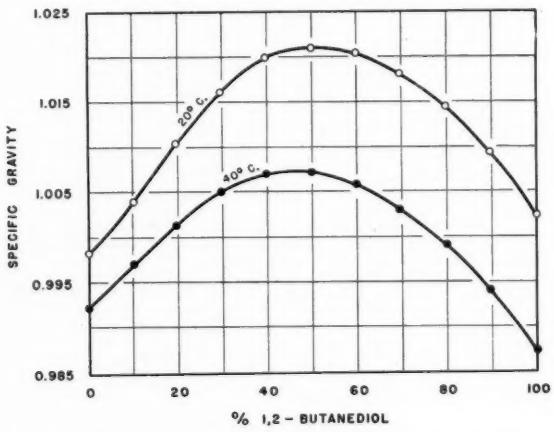

FIG. 3. *Specific gravity of aqueous 1,2-butanediol solutions at 20° and 40°C.*

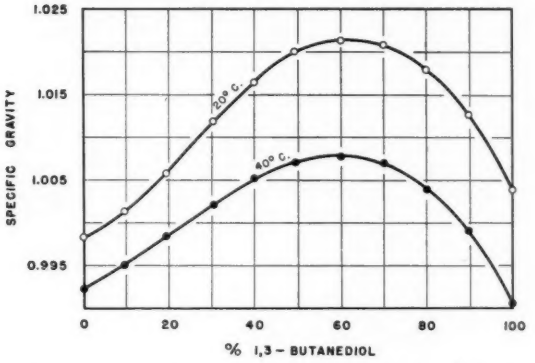

FIG. 4. *Specific gravity of aqueous 1,3-butanediol solutions at 20° and 40°C.*

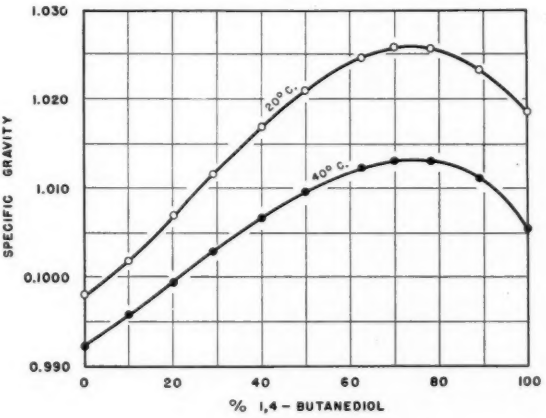

FIG. 5. *Specific gravity of aqueous 1,4-butanediol solutions at 20° and 40°C.*

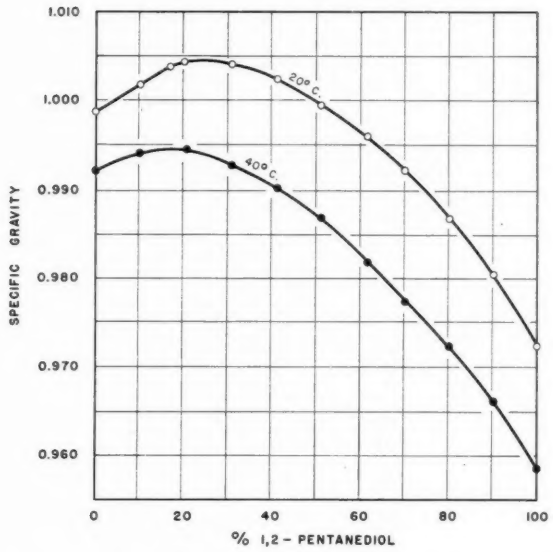

FIG. 6. *Specific gravity of aqueous 1,2-pentanediol solutions at 20° and 40°C.*

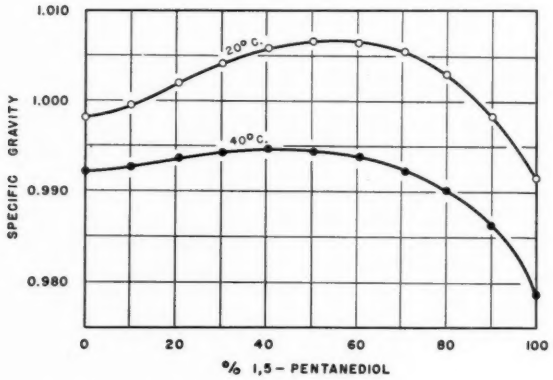

FIG. 7. *Specific gravity of aqueous 1,5-pentanediol solutions at 20° and 40°C.*

The isothermal contractions in volume which occur on mixing glycols with water (Table III) show large effects of position isomerism. Since maximum contraction for different diol isomers occurs at different diol concentrations, the maximum volume contraction rather than the contraction at uniform diol concentrations should be compared. In all three types of diol, isothermal contraction was largest in the 1,2-isomer, at both 20° and 40°C.

TABLE III

ISOTHERMAL CONTRACTION IN VOLUME ON MIXING GLYCOLS WITH WATER AT 20° AND 40°C.
(Ml. contraction per 100 ml. initial volume)

Glycol, %	1,2-Propanediol		1,3-Propanediol		1,2-Butanediol		1,3-Butanediol		1,4-Butanediol		1,2-Pentanediol		1,5-Pentanediol	
	20°C.	40°C.	20°C.	40°C.	20°C.	40°C.	20°C.	40°C.	20°C.	40°C.	20°C.	40°C.	20°C.	40°C.
20	0.83	0.86	0.37	0.29	1.12	1.01	0.69	0.65	0.70	0.58	1.125	0.95	0.52	0.43
40	1.84	1.58	0.90	0.81	1.96	1.67	1.58	1.36	1.10	0.86	1.49	1.22	1.04	0.80
60	2.08	1.79	1.19	1.07	1.92	1.65	1.94	1.64	0.98	0.76	1.38	1.06	1.23	0.98
80	1.47	1.30	1.01	0.89	1.27	1.10	1.50	1.29	0.59	0.46	0.97	0.735	1.01	0.88

Thermal expansion coefficients for the range 20°–40°C. are presented in Table IV. The aqueous solutions as well as the pure diols show progressively less thermal expansion, with increasing distance between the hydroxyl substituents. The differences in this property between glycols of differing chain length, but having the same distance between the hydroxyl groups (1,2-propanediol, 1,2-butanediol, 1,2-pentanediol), were smaller than those observed between different position isomers of the same molecular weight.

TABLE IV

THERMAL EXPANSION OF AQUEOUS GLYCOL SOLUTIONS BETWEEN 20° AND 40°C. ($\alpha \times 10^3$)

Glycol, %	1,2-Propanediol	1,3-Propanediol	1,2-Butanediol	1,3-Butanediol	1,4-Butanediol	1,2-Pentanediol	1,5-Pentanediol
20	0.40	0.39	0.454	0.390	0.375	0.50	0.415
40	0.61	0.47	0.645	0.557	0.50	0.61	0.57
60	0.695	0.55	0.726	0.675	0.645	0.72	0.64
80	0.67	0.60	0.765	0.702	0.645	0.75	0.65
100	0.71	0.61	0.775	0.666	0.646	0.72	0.65

The refractivity data of Tables V–VII show the deviations from linearity which are to be expected from the specific gravity data. Among the three types of glycol investigated, the refractivity as well as specific gravity increased regularly with the distance between the hydroxyl substituents.

Large effects of solvation become apparent when the logarithm of the viscosity of aqueous 2,3-butanediol solutions is plotted against diol concentration (4). This effect of solvation is so pronounced that the viscosity of aqueous *levo*-2,3-butanediol solutions is made appreciably higher than that

TABLE V

REFRACTIVE INDICES OF AQUEOUS PROPANEDIOL SOLUTIONS AT 20°, 30°, AND 40°C.

1,2-Propanediol				1,3-Propanediol			
Glycol, %	n_D^{20}	n_D^{30}	n_D^{40}	Glycol, %	n_D^{20}	n_D^{30}	n_D^{40}
9.94	1.3435	1.3422	1.3411	10.98	1.3433	1.3430	1.3410
20.03	1.3552	1.3540	1.3522	19.96	1.3540	1.3528	1.3511
30.23	1.3670	1.3650	1.3630	30.21	1.3654	1.3640	1.3623
40.01	1.3780	1.3758	1.3732	40.34	1.3770	1.3755	1.3735
49.41	1.3887	1.3863	1.3833	49.94	1.3880	1.3861	1.3839
60.04	1.3995	1.3970	1.3940	60.32	1.3997	1.3975	1.3951
69.50	1.4082	1.4055	1.4028	70.24	1.4103	1.4080	1.4065
79.43	1.4174	1.4144	1.4111	79.87	1.4205	1.4183	1.4155
89.74	1.4252	1.4221	1.4190	89.68	1.4300	1.4276	1.4250
100	1.4324	1.4295	1.4255	100	1.4389	1.4364	1.4332

TABLE VI

REFRACTIVE INDICES OF AQUEOUS BUTANEDIOL SOLUTIONS AT 20°, 30°, AND 40°C.

1,2-Butanediol				1,3-Butanediol				1,4-Butanediol			
Glycol, %	n_D^{20}	n_D^{30}	n_D^{40}	Glycol, %	n_D^{20}	n_D^{30}	n_D^{40}	Glycol, %	n_D^{20}	n_D^{30}	n_D^{40}
10.13	1.3452	1.3436	1.3420	9.51	1.3442	1.3430	1.3417	10.51	1.3444	1.3432	1.3420
19.69	1.3572	1.3553	1.3534	19.18	1.3552	1.3548	1.3520	20.01	1.3563	1.3550	1.3532
29.72	1.3693	1.3672	1.3650	30.20	1.3688	1.3670	1.3649	30.02	1.3682	1.3671	1.3659
39.79	1.3813	1.3788	1.3760	39.94	1.3800	1.3778	1.3755	39.86	1.3802	1.3790	1.3768
49.68	1.3920	1.3892	1.3865	49.45	1.3920	1.3895	1.3870	49.70	1.3935	1.3918	1.3898
59.88	1.4027	1.4000	1.3966	60.02	1.4040	1.4012	1.3983	59.95	1.4052	1.4042	1.4020
69.37	1.4120	1.4090	1.4058	70.10	1.4145	1.4118	1.4090	70.15	1.4183	1.4167	1.4140
79.73	1.4212	1.4185	1.4165	80.20	1.4242	1.4215	1.4185	79.85	1.4283	1.4258	1.4236
89.40	1.4297	1.4265	1.4230	89.67	1.4323	1.4295	1.4264	90.10	1.4370	1.4349	1.4318
100	1.4375	1.4347	1.4310	100	1.4398	1.4370	1.4331	100	1.4451	1.4425	1.4395

TABLE VII

REFRACTIVE INDICES OF AQUEOUS PENTANEDIOL SOLUTIONS AT 20° AND 40°C.

1,2-Pentanediol			1,5-Pentanediol		
Glycol, %	n_D^{20}	n_D^{40}	Glycol, %	n_D^{20}	n_D^{40}
10.36	1.3452	1.3430	10.17	1.3444	1.3420
19.97	1.3585		20.29		1.3543
20.64		1.3500	20.59	1.3572	
30.94	1.3705	1.3682	30.42	1.3700	1.3682
41.26	1.3830	1.3800	40.43	1.3833	1.3800
51.05	1.3930	1.3895	50.45	1.3960	1.3910
61.28	1.4050	1.3990	60.51	1.4080	1.4033
70.00	1.4120	1.4068	70.73	1.4198	1.4159
80.04	1.4223	1.4182	80.08	1.4304	1.4260
90.05	1.4320	1.4254	90.15	1.4417	1.4367
100	1.4390	1.4326	100	1.4500	1.4448

of aqueous glycerol solutions, at corresponding solute concentrations, over the range 10–50%. The magnitude of this solvation effect may be judged from the differences in viscosity of pure glycerol and pure *levo*-2,3-butanediol (1500 c.p. and 56 c.p. respectively at 20°C.).

The absolute and kinematic viscosities of the pure butanediols do not bear a simple relation to the distance between the hydroxyl substituents (Figs. 8–10, Table VIII). *levo*-2,3-Butanediol is less viscous, and *meso*-2,3-butanediol

TABLE VIII

KINEMATIC VISCOSITY OF AQUEOUS BUTANEDIOL SOLUTIONS AT 20° AND 40°C.
(Data are expressed in centistokes)

1,2-Butanediol			1,3-Butanediol			1,4-Butanediol		
Glycol, %	Viscosity		Glycol, %	Viscosity		Glycol, %	Viscosity	
	20°C.	40°C.		20°C.	40°C.		20°C.	40°C.
10.125	1.520	0.910	9.505	1.51	0.91	10.51	1.446	0.89
19.69	2.187	1.243	19.175	2.295	1.291	20.01	2.109	1.218
29.72	3.310	1.690	30.20	3.529	1.818	30.02	2.867	1.6602
39.79	4.802	2.311	39.94	5.419	2.593	39.86	4.258	2.382
49.685	6.739	3.088	49.45	8.313	3.695	49.70	6.57	3.202
59.88	9.72	4.227	60.02	13.44	5.600	59.95	10.20	4.707
69.37	13.82	5.744	70.1	21.57	8.413	70.15	18.48	7.982
79.73	21.37	8.372	80.20	35.36	12.88	79.85	30.63	12.62
89.40	35.54	12.57	89.67	63.43	21.21	90.1	54.35	21.40
100	68.0	21.25	100	129.8	39.70	100	87.62	33.8

is more viscous than 1,2-butanediol, although the hydroxyls are on adjacent carbon atoms in all three compounds. Michael and Hopkins (12) have previously referred to the high viscosity of 1,3-butanediol. The present and earlier data (3) show that its viscosity in the absence of water is much higher than that of 1,2-, 1,4-, and *levo*-2,3-butanediol. The effect of position isomerism on the viscosity of pure diols is thus a discontinuous one. The viscosity of pure 1,5-pentanediol is almost twice as high as that of 1,2-pentanediol (Figs. 11–12, Table IX), expressed in either absolute or kinematic units. Judging from the

TABLE IX

KINEMATIC VISCOSITY OF AQUEOUS PENTANEDIOL SOLUTIONS AT 20° AND 40°C.
(Data are expressed in centistokes)

1,2-Pentanediol			1,5-Pentanediol		
Glycol, %	Viscosity		Glycol, %	Viscosity	
	20°C.	40°C.		20°C.	40°C.
10.36	1.5475	0.9275	10.17	1.516	0.9210
19.97	2.264	1.258	20.09	2.246	1.277
30.18	2.88	1.538	30.42	3.300	1.795
40.13	4.06	2.08	39.82	4.735	2.331
50.02	5.73	2.82	50.04	7.08	3.350
59.96	8.02	3.742	60.12	11.30	5.250
69.97	13.03	5.725	70.45	20.9	8.842
79.85	19.85	8.138	80.20	36.22	14.46
90.05	38.20	13.62	89.75	66.25	25.70
100	68.55	20.82	100	115.65	43.58

butanediol data, 2,3-, and 3,4-pentanediols should have lower viscosities than 1,2-pentanediol, whereas the viscosities of the 1,3- and 1,4-pentanediols would be expected to be higher.

The viscosity–diol concentration data for aqueous butanediol and pentanediol solutions show largest solvation effects for the 1,2- and 2,3-diols, which are the least associated or lightest in the pure state (3) (Figs. 8–12, Tables VIII–IX). This interaction of solvation and position isomerism effects is best shown by the butanediols. In the absence of water, the order of increasing viscosity is *levo*-2,3-, 1,2-, and 1,4-butanediol; in the presence of 50–80% water, at 20°C., the order of the viscosities is reversed, although the differences in viscosity of the aqueous solutions are small. At 40°C., the aqueous solutions of these three butanediols have almost identical viscosities. 1,3-Butanediol solutions were more viscous than any other type of butanediol solution at all concentrations and temperatures tested. Aqueous 1,5-pentanediol solutions were consistently more viscous than the 1,2-pentanediol solutions. The viscosities of these two systems were similar in magnitude to those of the 1,2- and 1,4-butanediols.

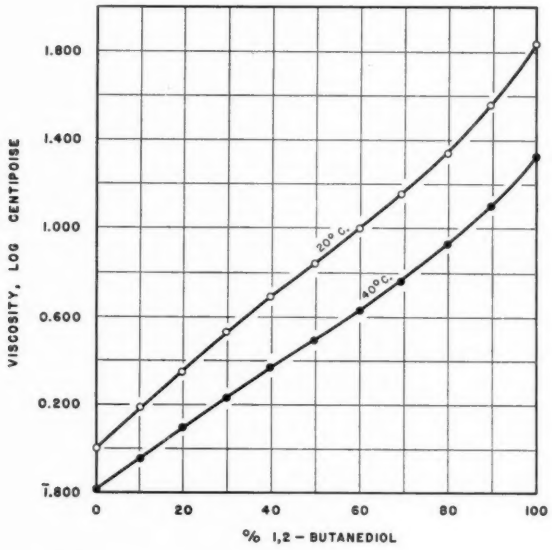

FIG. 8. *Absolute viscosity of aqueous 1,2-butanediol solutions at 20° and 40°C.*

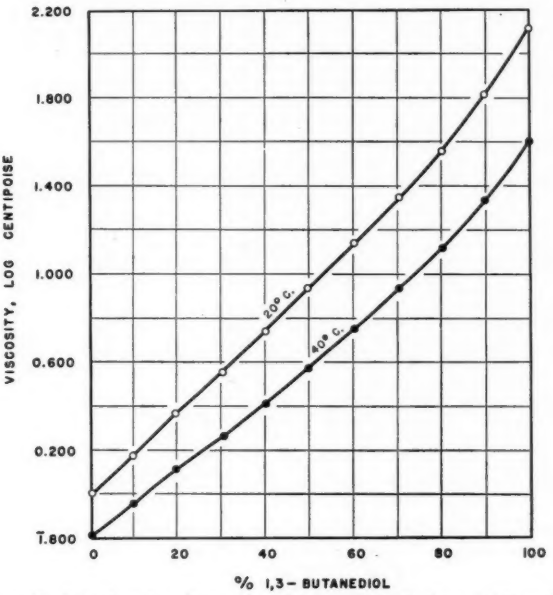

FIG. 9. *Absolute viscosity of aqueous 1,3-butanediol solutions at 20° and 40°C.*

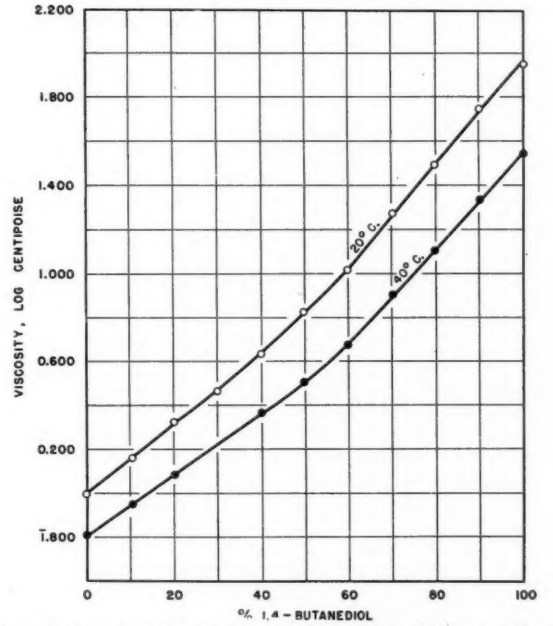

FIG. 10. *Absolute viscosity of aqueous 1,4-butanediol solutions at 20° and 40°C.*

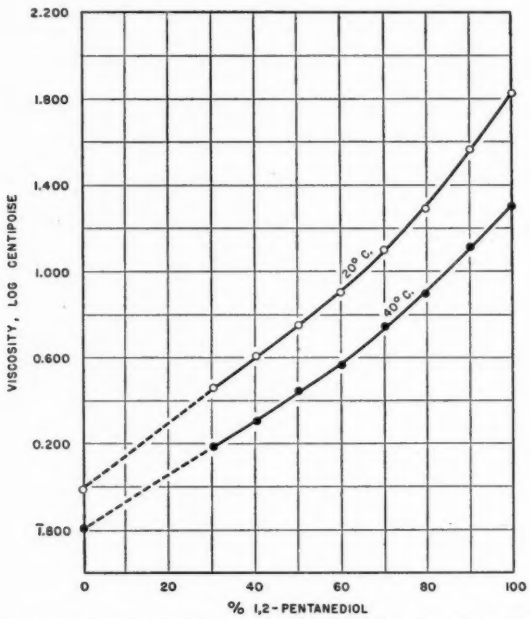

FIG. 11. *Absolute viscosities of aqueous 1,2-pentanediol solutions at 20° and 40°C.*

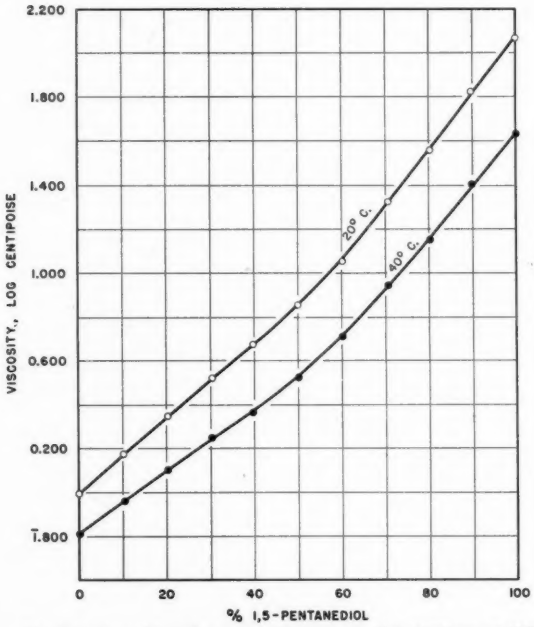

FIG. 12. *Absolute viscosities of aqueous 1,5-pentanediol solutions at 20° and 40°C.*

The effectiveness of the eight diols as freezing point depressants decreases in the following order (Table X) at a concentration of 60%: 1,2-propanediol, *levo*-2,3-butanediol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,2-butanediol, 1,5-pentanediol and 1,2-pentanediol. It is noteworthy that *levo*- (or *dextro*-) 2,3-butanediol is more effective in this respect than any other type of

TABLE X

FREEZING POINTS OF AQUEOUS PROPANEDIOL, BUTANEDIOL, AND PENTANEDIOL SOLUTIONS, °C.

Glycol, %	1,2-Propanediol	1,3-Propanediol	1,2-Butanediol	1,3-Butanediol	*levo*- 2,3-Butanediol	1,4-Butanediol	1,2-Pentanediol	1,5-Pentanediol
10	− 3.12	− 2.86	− 2.60	− 2.34	− 3.1	− 2.30	− 2.3	− 2.3
20	− 7.6	− 6.5	− 6.0	− 5.2	− 7.1	− 5.48	− 4.8	− 4.9
30	−14.0	−11.8	−11.0	−10.5	−12.4	−10.0	− 6.8	− 8.4
40	−22.7	−18.8	−16.5	−16.8	−19.4	−14.8	− 8.4	−11.3
50	−34.5	−27.7	−22.4	−25.2	−29.6	−22.0	−10.2	−15.3
60	−48.2	−40.0	−29.0	−35.3	−40.4	−31.3	−12.6	−21.0

butanediol. Freezing point lowering by glycols does not bear a simple relation to the distance between the hydroxyl substituents, at least among the butanediols; *levo*-2,3-butanediol is much more effective than 1,2-butanediol, which also has the hydroxyls on adjacent carbon atoms; 1,3-butanediol shows a significantly greater freezing point lowering than either the 1,2- or 1,4-butanediols. The original Hibbert patent (9), covering the use of glycols in general as antifreeze compounds, draws particular attention to the usefulness of 1,2-diols, irrespective of chain length. From Table X, it is apparent that 1,2-propanediol is superior to 1,3-propanediol in this respect; however, 1,2-butanediol and 1,2-pentanediol are less effective as freezing point depressants than any other examined isomer of butanediol and pentanediol respectively, with the exception of *meso*-2,3-butanediol.

Summary and Conclusions

It is now apparent that the distance between hydroxyl substituents in propanediols, butanediols, and pentanediols influences the density, refractivity, boiling point, thermal expansion, and isothermal contraction on mixing in a quite regular manner, regardless of the chain length. As might be expected, the most striking effects were observed in the pentanediols, and these were similar in kind to the effects observed on the propanediols and butanediols. A simple relation to hydroxyl position was not observed for freezing point lowering and viscosity. The glycol isomers, which are lightest and least viscous in the anhydrous state, exhibit greatest contraction on mixing with water, with the result that the differences in viscosity of the pure isomers are lessened or abolished in aqueous solution. *levo*-2,3-Butanediol is more effective as a freezing point depressant than any other butanediol isomer, and falls between 1,2-propanediol and 1,3-propanediol with respect to this property. The glycol concentration at which maximum specific gravity in the presence of water is shown among the propane-, butane-, and pentanediols is very markedly influenced by position isomerism. It has previously been shown that the stereoisomers of 2,3-butanediol attain specific gravity maxima at the same glycol concentration.

The present study has dealt with only a few physical properties of glycol position isomers; many additional properties await investigation, and those which have been considered in this paper appear worthy of further attention.

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THE MECHANISM OF OXYMERCURATION OF ALKENES[1]

By A. G. Brook and George F Wright

Abstract

A factual test of several possible mechanisms by which alkenes are oxymercurated shows that while addition of mercuric acetate to cyclohexene can be effected smoothly, this 1-acetoxy-2-acetoxymercuricyclohexane cannot be an intermediate in the conversion of cyclohexene in methanolic mercuric acetate to 1-methoxy-2-acetoxymercuricyclohexane. The rate at which the first compound is converted to the second in methanol is much too slow to account for the rate of methoxymercuration. Indeed the behavior of conversion indicates that the first compound reverts in methanol to cyclohexene which then combines with the elements of methoxymercuric acetate. Ionic mechanisms have been shown to be untenable since hydroxymercuration is slower than methoxymercuration although it occurs in a solvent which is much more polar than methanol. A co-ordinative dipole mechanism is suggested which explains the complete retention of configuration during addition as well as the function of boron trifluoride as an accelerator in this reaction.

When an alkene is treated with mercuric acetate in a hydroxylated medium, a reaction occurs which may be illustrated as follows:

$$Hg(OAc)_2 + \begin{array}{c} R_1 \quad R_3 \\ | \quad | \\ C{=}C \\ | \quad | \\ R_2 \quad R_4 \end{array} \xrightarrow[-HOAc]{+ROH} \begin{array}{c} R_1 \quad R_3 \\ | \quad | \\ RO{-}C{-}C{-}HgOAc. \\ | \quad | \\ R_2 \quad R_4 \end{array}$$

Each of the groups (RO and HgOAc) which are added to the alkene occupies the indicated position if R_1 and R_3 are hydrogen and R_2 is phenyl while R_4 may be methyl (15), benzoyl (11), carboethoxy (15), cyano (6), or hydrogen (15); only in the methoxymercuration of oleic and elaidic acids where R_2 and R_4 are very similar are positional isomers evident (7). Furthermore if the alkene is capable of geoisomerism (R_1, R_3 = H; $R_2 \neq R_4$) the *cis* or *trans* form each yields its characteristic diastereoisomer uncontaminated with the other (3, 6, 15). The mode of addition has been found in one instance (cyclohexene, where R_1, R_3 = H and $R_2 + R_4 = -(CH_2)_4-$) to be *trans*, i.e., to involve a Walden inversion at one of the two alkene carbon atoms (5).

The reactions which diastereomeric oxymercurials undergo are few and not structurally definitive. Bromination or iodination yields the 1-oxy-2-halogeno analogue but stereochemical configuration is lost during these processes (6). This loss of configuration is, of course, generally characteristic whenever a metal is substituted on, or removed from, a carbon atom. In at least one instance (14) configuration is also lost if the equilibrium $RHgX \rightleftarrows R_2Hg + HgX_2$ is established. The unstable R_2Hg derivatives have not been isolated (3) except in one case (1) when a difficultly separable mixture of stereoisomers could not have been produced because the double bond in the parent alkene was terminal. The oxymercuration process is reversed in mineral acid;

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the alkene thus regenerated tends toward an equilibrium mixture of the two possible geoisomers. However, in one instance D. C. Downing in this laboratory was able to obtain nearly pure *cis* stilbene by cold hydrochloric acid treatment of the *dd,ll*-1-methoxy-2-chloromercuri-1,2-diphenylethane which was prepared from the same geoisomer.

Although the two 1-methoxy-2-chloromercuricyclohexanes have been distilled *in vacuo* all 1-oxy-2-organomercuric salts ionize to some extent in water. The acetate, chloride, bromide, iodide, hydroxide, and benzoate anions are mutually interchangeable in these salts without alteration in the cationic stereoconfiguration. The acetate salts of most oxymercurials are slightly soluble in water, while the weakly basic 1-oxy-2-organomercuric hydroxides are usually very soluble. Since the water-insoluble salts are thus usually soluble in alkali, the exchange of anion is frequently accomplished by appropriate neutralization of the hydroxides.

The over-all kinetic behavior of oxymercuration is second order in excess of the hydroxylated solvent medium, according to a convenient analysis for unchanged mercuric acetate (7, 15). Indeed this analysis can be used to evaluate the composition of geoisomeric mixtures (7) since the *cis* alkene always reacts more rapidly than its *trans* geoisomer (2). Precaution must be taken, however, to eliminate oxygen and organic peroxides because the oxymercuration reaction is strongly catalyzed by such substances. Decay of rate constant shows that such catalysts disappear during the reaction (14). This peroxide catalyst probably does not involve a free radical mechanism of oxymercuration. It has indeed been shown that phenyl radicals cause the equilibration of the two diastereomeric 1-methoxy-2-chloromercuricyclohexanes, yet only one diastereomer is obtained from a peroxide-catalyzed reaction involving a single geometric isomer.

Furthermore some oxymercuration reactions are strongly catalyzed by boron trifluoride which is electrophilic in its catalytic action. Catalysis would thus seem to be a function of electron acceptance, especially since electron donors such as pyridine or various nitriles have strong inhibiting action, stoichiometrically related to the acceleration due to boron fluoride.

Methanol is the most commonly used hydroxylic solvent for oxymercuration since the reaction is more rapid in this medium than in the higher alcohols, and products are obtained which are less contaminated with by-products. For example the second-order rate constant for methoxymercuration of cyclohexene is 30.3×10^{-2} liters. millimole^{-1}. sec.$^{-1}$ at concentrations 10^{-3} molar while that for the ethoxymercuration (2.5×10^{-3} molar) is 0.67×10^{-2} and it decays badly after the reaction is about 75% completed. This decay is more severe than that encountered in methoxymercuration and it cannot be owing to decomposition of peroxide, since this catalyst was absent. Methanol is a better solvent for mercuric acetate than the higher alcohols. Thus tertiary butyl alcohol does not dissolve mercuric acetate, and a heterogeneous mixture of the two with cyclohexene does not react appreciably over a day

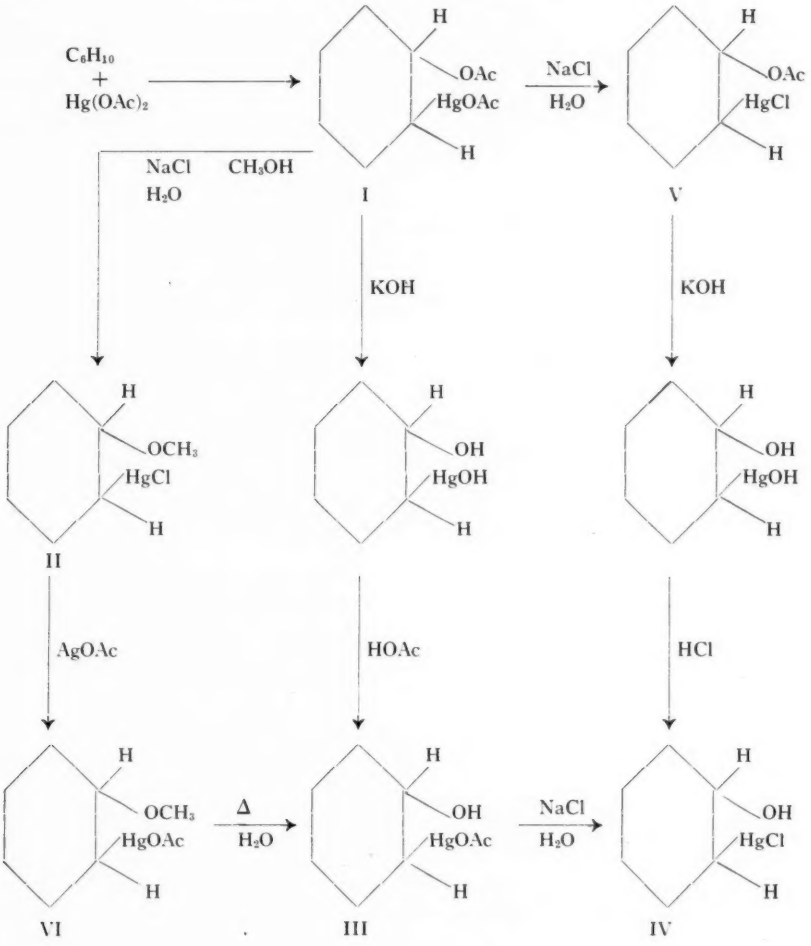
unless boron fluoride is added. With this catalyst a 50% yield of 1-*tert*-butoxy-2-chloromercuricyclohexane is obtained after treatment with sodium chloride.

Since the rate of oxymercuration increases as the alcohol used in the reaction becomes simpler, one might expect that the reaction would be faster in water than in any alcohol, although this conclusion would be inconsistent with the reliability of the analytical method used in kinetic studies of the reaction. Actually a rate study cannot be effected in water owing to the insolubility of cyclohexene in this medium. However, an evaluation can be made by allowing a mixture of water and methanol to compete for mercuric acetate in presence of 1 equivalent of cyclohexene. The composition of the product, converted to chloromercurials, has been ascertained by thermal analysis with a temperature–composition diagram. Since 60–80% of the product was found to be 1-methoxy-2-chloromercuricyclohexane it is evident that hydroxymercuration is a slower process than methoxymercuration. On the other hand a similar competition between ethanol and water shows that ethoxymercuration is slower than hydroxymercuration, so the rate of hydroxymercuration presumably lies between the limits 3.03 and 0.67×10^{-2} for methanol and ethanol respectively.

The preparations of 1-ethoxy-2-chloromercuricyclohexane and 1-hydroxy-2-chloromercuricyclohexane (IV) were carried out exactly like the similar methoxymercuration and all three give yields over 95% of theoretical. The yield of 1-hydroxy-2-acetoxymercuric acetate, which must be obtained by chloroform extraction of the aqueous reaction mixture, has never been raised above 76% of theoretical.

The preparation of 1-hydroxy-2-acetoxymercuricyclohexane (III or its chloromercuri analogue, IV) could also be effected, in quantitative yield, when a solution of *dd,ll*(*trans*) 1-methoxy-2-acetoxymercuricyclohexane (II, formerly called alpha) in water was boiled 30 min. When *dl,ld* (*cis*) 1-methoxy-2-acetoxymercuricyclohexane was prepared anew from the known (beta) diastereomeric chloromercurial and was subjected to treatment with water at temperatures as high as 150°C. it was recovered unchanged, even when 2% of aqueous alkali was added. More strenuous treatment gave metallic mercury in partial or total yield. It was thus impossible to ascertain by these experiments whether a diastereomeric 1-hydroxy-2-acetoxymercurial could be formed in this manner. At this time an unequivocal configuration cannot be assigned, therefore, to mercurials III and IV. The marked stability of *dl,ld* (*cis*) 1-methoxy-2-acetoxymercuricyclohexane, as contrasted to its *dd,ll* (*trans*) diastereomer (5, 14), would indicate that the latter was converted to III by a reversal of the methoxymercuration reaction which would be followed by a hydroxymercuration of alkene.

The mechanism by which the oxymercuration proceeds may be described in several ways (15). One of these might involve the initial addition of mercuric acetate to the alkene, followed by replacement of the acetate radical



by that of the solvent medium. Thus mercuric acetate and cyclohexene might react to form 1-acetoxy-2-acetoxymercuricyclohexane (I). This subsequently would be converted by methanol to the 1-methoxy derivative, most conveniently isolated after treatment with aqueous sodium chloride as 1-methoxy-2-chloromercuricyclohexane II. Such a reaction might be expected to be second-order in excess of methanol.

Although some addition compounds comprising mercuric acetate and alkene have been reported (9), these examples did not include 1-acetoxy-2-acetoxymercuricyclohexane. It was found later (14) that mercuric acetate was taken up by cyclohexene over a period of days. While this reaction rate

was much slower than that of methoxymercuration of cyclohexene, the initial mixture of cyclohexene and mercuric acetate was heterogeneous. Comparison of rate with that of the homogeneous system from which 1-methoxy-2-acetoxymercuricyclohexane was formed would therefore have little meaning. It seemed then worthwhile to prepare authentic 1-acetoxy-2-acetoxymercuricyclohexane and to ascertain its behavior, especially in methanol.

Although the rate at which mercuric acetate adds to cyclohexene is very slow it can be accelerated markedly by inclusion of 0.1 mole equivalent of boron fluoride or a peroxide. The suspension in petroleum ether is converted almost quantitatively to 1-acetoxy-2-acetoxymercuricyclohexane, I. This compound begins to decompose a few minutes after it is isolated, but it can be converted to the corresponding chloromercurial, V, if its solution in methanol is poured quickly into dilute aqueous sodium chloride solution. It consumes only 1 equivalent of thiocyanate (15).

This chloromercurial V can also be prepared from cyclohexene and mercuric acetate in acetic acid (with subsequent dilution into aqueous sodium chloride) but the yield is little better by this method of Hugel and Hibou (9) than that obtained in petroleum ether medium. The method of preparation (85% yield), when quantities are required, involves the use of eight moles of acetic anhydride and four moles of cyclohexene per mole of mercuric acetate. This reaction mixture is homogeneous at steam-bath temperature. The reaction is sufficiently rapid that no catalyst, such as boron fluoride, is required.

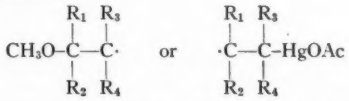
Either of the compounds I and V dissolves in dilute alkali with considerable decomposition. Mercuric oxide must be filtered off and the solution smells strongly of cyclohexene. Careful acidification yields some 1-hydroxy-2-acetoxymercuricyclohexane III or the corresponding chloromercurial IV depending on whether acetic or hydrochloric acid is used. Since the conditions of reaction are approximately those used for hydroxymercuration of cyclohexene, the preparation of III and IV from I or V cannot be considered to involve simple replacement of an acetoxy by a hydroxy group.

Methanol does not react appreciably with 1-acetoxy-2-acetoxymercuricyclohexane I over the few minutes required for complete methoxymercuration of cyclohexene (14) but after seven hours the conversion to *dd,ll* (*trans*) 1-methoxy-2-acetoxymercuricyclohexane is evidently complete. This is confirmed by the quantitative yield of the chloromercurial II after treatment of the methanolic solution with aqueous sodium chloride. It may thus be seen that, although mercuric acetate will add to cyclohexene in good yield and the product, I, can be converted to the methoxymercurial (II or VI) in good yield, the rate of either reaction is very much slower than that found for direct methoxymercuration. The mechanism suggested above for methoxymercuration must therefore be invalid.

Evidence can indeed be presented to show that the apparent exchange of acetoxy for methoxy outlined above probably does not occur at all in the sense

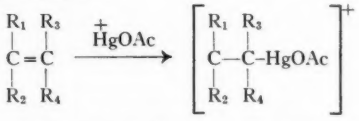
of this mechanism, but is instead a decomposition to the alkene followed by a resynthesis. Thus it is known that methoxymercuration is a process involving formation of acetic acid which depends for completeness on low final acid concentration (15). Typically, treatment of cyclohexene with methanolic mercuric acetate is practically quantitative, whereas the similar reaction with chloromercuric acetate does not yield over 10% of methoxychloromercuricyclohexane and the reaction is very slow. Now when 1-acetoxy-2-chloromercuricyclohexane V is dissolved in methanol and the solution is poured into aqueous sodium chloride after 30 min., none of the methoxymercurial II can be isolated, though an 8% yield is obtained when the methanolic solution is held over four hours. In either case an immediate precipitate of mercuric oxide (distinguishable from the slow precipitation from 1-hydroxy-2-acetoxymercuricyclohexane, III) is formed when the aqueous diluate is treated with alkali. These experiments indicate strongly that 1-acetoxy-2-chloromercuricyclohexane I decomposes in methanol to cyclohexene and chloromercuric acetate. This system then must react slowly and incompletely to give the methoxychloromercurial, II.

Since a mechanism involving acetoxyorganomercuric acetate thus seems to be inapplicable, consideration may be given to fragmentary additions of the radical or ion type. It has already been pointed out that the first of these (radical type) is improbable because of the fact that free radicals are known in at least one instance to cause equilibration of the two possible diastereoisomeric oxymercurials, whereas in fact only one diastereomer is obtained from each of a pair of geoisomers. Furthermore no instance is known where configurational identity is retained when the intermediate is a free radical arising from one of a pair of radical fragments.



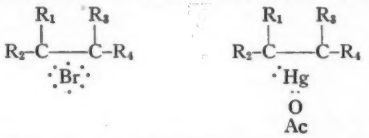
Finally the fact that oxymercuration is accelerated by boron trifluoride indicates that the reaction does not proceed by a radical mechanism.

Similar objections apply to ionic mechanisms to explain oxymercuration. The uncatalyzed addition of mercuric ion to an alkene would involve the formation of a carbonium ion.



There is no authenticated evidence that a carbonium ion can retain pyramidal form sufficiently at normal collision rate to retain the configuration required for production of a single diastereomer from a geoisomer. Attempts have been made to define such a carbonium ion, by analogy with the bromonium ion of Roberts and Kimball (13), as a resonance hybrid which is called an ethylene-

mercurinium ion (10), but the analogy would seem to be meaningless as a device for the explanation of configuration retention. The justification for the postulated alkenebromonium ion depends on unshared electron pairs on the bromine atom which preserve the tetrahedral configuration at the carbon atoms. The mercury atom has no valence electrons with which to accomplish



this co-ordinative binding, nor can it enjoy configurational integrity simply by calling it a "resonating" ion. Indeed a resonance hybrid might be expected to produce positional isomers which ordinarily are not encountered during oxymercuration.

Furthermore the existence of an organomercury ion during the process of oxymercuration ought to depend, as do all metallic electropositive ions in solution, on the polarity of the solvent. On this basis it might be expected that oxymercuration would proceed more rapidly in water than in methanol which has a much lower dielectric constant. Actually the reaction is slower in water than in methanol. There seems then to be no justification for postulate of an electropositive free ion intermediate.

Retention of configuration during normal collision rate might be more probable in an anionic intermediate induced by addition of a methoxide ion. But this ion energetically cannot stabilize itself by complex formation with an alkene. Under any circumstances the concentration of methoxide ion in a methanolic solution of mercuric acetate must be negligible, since ion transport between electrodes with a 62 volt potential difference was barely detectable, although appreciable transport is obtained in a water solution of mercuric acetate wherein oxymercuration is a relatively slow reaction.

Since oxymercuration seems not to occur through an intermediate addition of mercuric acetate, and radical or ionic mechanisms cannot explain the kinetic and structural characteristics of the reaction, there remains only the possibility that addition occurs through co-ordinative dipole formation. It is characteristic of a solution of mercuric acetate in water, and more so in methanol, that it hydrolyzes with release of acetic acid.

$$Hg(OAc)_2 + CH_3OH \rightleftharpoons CH_3OHgOAc + HOAc\,.$$

Although the methoxymercuric acetate cannot be isolated from such a system it must certainly be present, and we have postulated it as the addend in the oxymercuration reaction. Two modes of initial attack are possible, but if the mercury atom were initially to co-ordinate with the π electron pair of the alkene then either racemization of the unoccupied carbon atom would take place (with loss of configuration) or else the spatially most probable contiguous addition of methoxyl should occur with resultant *cis* configuration of the

oxymercurial. Since this is contrary to fact it remains to examine the consequences of initial co-ordination via the unshared electron pair on the methoxyl oxygen.

This may be illustrated by the addition of methoxymercuric acetate to *cis*-stilbene (15). Attack of the face C_6H_5-*b*-H of the lower tetrahedron of I by the electron pair of the methoxy oxygen in methoxymercuric acetate would displace the electron pair at *a* entirely to the upper tetrahedron while configurational inversion occurred at the lower tetrahedron. The upper tetrahedron would retain its configuration in II because of the electron pair which it acquired, until rotation could occur within this dipole. Such rotation would bring this electron pair close enough in III to appropriate the acetoxymercuri fragment from the methoxyl oxygen and to complete the formation of the *dd* (or *ll*) methoxymercurial, IV. A similar type of addition to *trans* stilbene, I′, would form the *dl* (or *ld*) 1-acetoxymercuri-2-methoxy-1,2-diphenylethane.

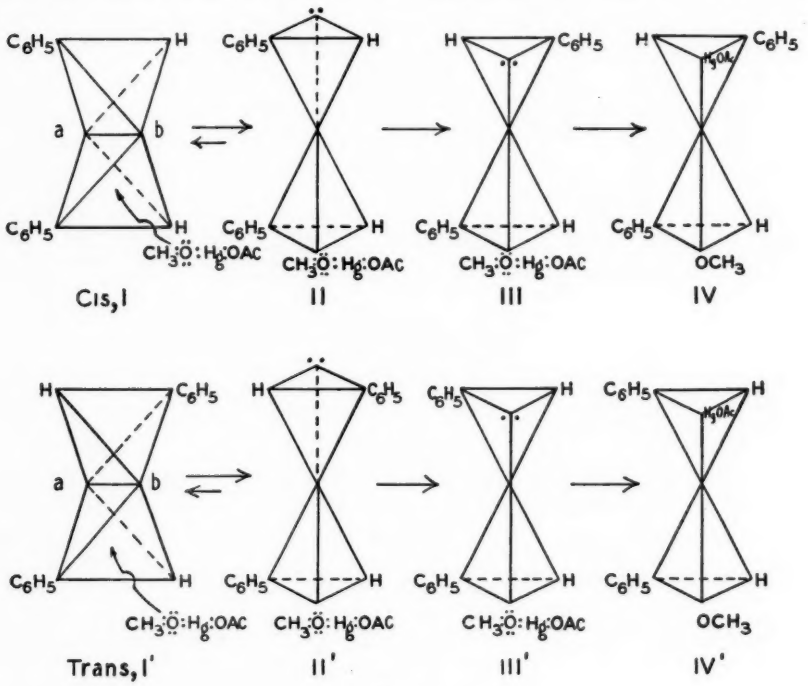


FIG. 1.

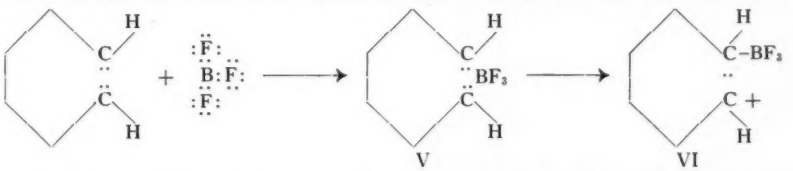
If this proposal of mechanism is valid it must explain the fact that the *cis* isomer, I, always methoxymercurates faster than the *trans*, I′. It should be understood that the formulation I → IV represents a collision between two molecules which will culminate into reaction insofar as the activated complex

can be inactivated by formation of the product IV. Steps to II and III represent the stages through which this inactivation process must occur. But the conversion of II to III involves less decrease in symmetry than does conversion of II′ to III′ since centrosymmetry is approximated in II → III but only planosymmetry is approximated in II′ → III′. In consequence reaction following collision in the case of *cis*-stilbene ought to be more efficient than when *trans*-stilbene collides with methoxymercuric acetate. The marked difference in the force-fields of phenyl and hydrogen which contribute to this symmetry argument may account for the great difference in rate of methoxymercuration of these two geoisomers.

Any postulated mechanism for oxymercuration must explain the fact that the reaction is accelerated by presence of substances like boron fluoride or organic peroxides, each of which is specifically advantageous for certain alkenes, and must explain the more general inhibition when pyridine or nitriles are added. Furthermore the explanation should include the observation (2) that the electron-accepting accelerators and the electron-donating inhibitors do not act independently but can compensate one another.

A discussion of the catalytic activity of organic peroxides must be deferred until more is known about such activity when a free-radical mechanism is improbable, as in the present case. Certainly the action of peroxides in reactions such as the Cannizzaro which are predominantly ionic or dipolar in nature is not yet clearly understood. It is of course evident from the stoichiometric composition of organic peroxides that they originally form by coordinative dipole interaction of molecular oxygen with alkenes, but little is known otherwise.

On the other hand the catalytic activity of the more powerful catalyst, boron trifluoride, is well understood. Specifically this substance is catalytic both for oxymercuration and for polymerization of cyclohexene. In its capacity as the polymerizing agent for alkenes, boron trifluoride must evidently be acting as a polarizer where V represents the "π complex" and VI an activated



V VI

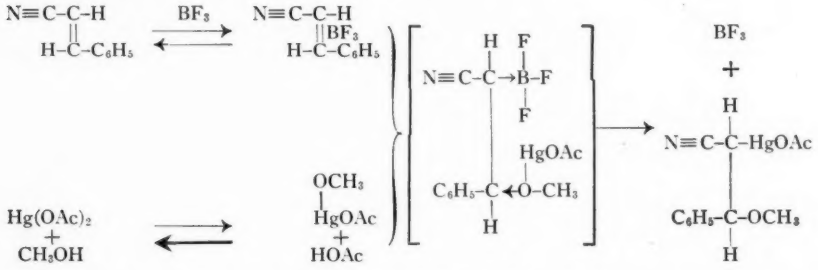
state. The postulate of these two states is justified on the basis that addition of boron trifluoride to *trans*-stilbene at room temperature is not in itself sufficient to cause the isomerization which might be expected in the activated state VI (8, 12). Similarly boron trifluoride in methanol was found not to cause isomerization of either *cis* or *trans* styryl cyanide (3).

The polymerization catalysis of cyclohexene is inhibited by addition of acetonitrile, and especially by the addition of pyridine to much the same extent

as these substances inhibit oxymercuration. This might be attributed to capture of the electron-accepting boron fluoride by the electron-donating pyridine.

On the other hand oxymercurations have been reported (3) wherein pyridine and nitriles inhibited reactions which ostensibly were uncatalyzed. This inhibition might, however, be expected in view of the tendency for nitrogen compounds (and especially pyridine) to co-ordinate with mercuric salts to yield isolable compounds of type $HgX_2.2C_5H_5N$. In either event the inhibition by pyridine or nitriles would not be specific to the alkene used, in contrast to the specific acceleration by peroxides or boron fluoride. This specificity is apparent in the fact that, although the methoxymercurations of the styryl cyanides and cyclohexene are catalyzed both by organic peroxides and by boron trifluoride, the methoxymercuration of benzalacetophenone is catalyzed by boron trifluoride but not appreciably by peroxide. Conversely *trans*-stilbene will methoxymercurate in presence of peroxide but not of boron fluoride.

In summary the mechanism of oxymercuration may be illustrated by the boron fluoride – catalyzed methoxymercuration of *trans*-styryl cyanide, wherein the catalyst is shown to facilitate energy transfer by conversion of an addition reaction into one that is metathetical.



This formulation, like that which could be written for benzalacetophenone, might also show an initial co-ordination of boron trifluoride with the cyano group. Such a representation would not alter the concept that the electron-accepting catalyst acts by promoting co-ordinative Walden inversion at the carbon atom to which the phenyl group is attached.

Experimental*

1-Acetoxy-2-acetoxymercuricyclohexane

A suspension of 20 gm. (0.063 mole) of mercuric acetate in 8 ml. (0.08 mole) of cyclohexene and 10 ml. of petroleum ether (b.p. 60–70°C.) was stirred

**All melting points have been corrected against reliable standards.*

rapidly for seven hours at 35°C. A white solid appeared as a cake on the flask wall. This cake was scraped out, washed with petroleum ether, and dried to yield 23 gm. of 1-acetoxy-2-acetoxymercuricyclohexane, m.p. 86–89°C. Because of its instability this 91% crude yield was analyzed at once. Calc. for $C_{10}H_{16}O_4Hg$: % Hg, 50.1. Found: % Hg, 51.3.

When 0.003–0.006 mole of boron fluoride etherate or nitric acid was included with the reagents the reaction time was decreased to one hour. The catalysis did not affect the quality of product. The original white powder became sticky after five minutes and gave a strong odor of cyclohexene and acetic acid. These volatile substances were found to be approximately equimolar when they were condensed as 17% of the weight of the white powder while it was maintained under vacuum for 12 hr.

1-Acetoxy-2-chloromercuricyclohexane

A. From the Acetoxymercurial

When 5 gm. (0.0125 mole) of 1-acetoxy-2-acetoxymercuricyclohexane was dissolved in methanol and filtered into dilute aqueous sodium chloride an oil formed. This slowly crystallized to yield 3 gm. (65% yield) of 1-acetoxy-2-chloromercuricyclohexane, m.p. 96–98°C.

B. From Mercuric Acetate

A solution of 20 ml. (0.2 mole) of cyclohexene in 37 ml. (0.4 mole) of acetic anhydride was heated with 15.9 gm. (0.05 mole) of mercuric acetate on the steam bath for 30 min. The solution was then filtered into 200 ml. of 2% aqueous sodium chloride solution. The resulting oil slowly crystallized to yield 16 gm. (85 mole %) of 1-acetoxy-2-chloromercuricyclohexane, m.p. 91°C. This melting point was raised to 102–103°C. by crystallization from acetone or butanone-2 or by solution in acetone (6 ml. per gm.) followed by dilution with 4% aqueous sodium chloride (8 ml. per gm.). Calc. for $C_8H_{13}O_2HgCl$: C, 25.4; Hg, 53.2; Cl, 9.42; CH_3CO, 11.4%. Found: C, 25.4; Hg, 53.3; Cl, 9.43; CH_3CO, 11.7%.

While this chloromercurial is more stable than the acetoxy-analogue it will decompose slowly at 25°C. At 90°C. under 15 mm. it loses 25% of its weight in two hours. The volatile condensate consists approximately of equimolar quantities of acetic acid and cyclohexene.

dd,ll (trans) 1-Methoxy-2-chloromercuricyclohexane

A solution or 3 gm. (0.0075 mole) of 1-acetoxy-2-acetoxymercuricyclohexane in 20 ml. of absolute methanol was maintained for seven hours, then filtered into stirred dilute aqueous sodium chloride. The *dd,ll* (*trans*) methoxychloromercurial which was filtered off weighed 2.6 gm. (99% yield), m.p. 109–113°C. After purification to melt at 114–116°C. this compound was identified by mixed melting point. When the reaction time in methanol was 30 min., the chloromercurial yield was 47%; after three minutes reaction time none was produced.

When 0.3 gm. (0.0075 mole) of 1-acetoxy-2-chloromercuricyclohexane was shaken for 10 min. in 18 ml. of methanol it dissolved completely. After 20 min. longer when the solution was poured into dilute aqueous sodium chloride no methoxychloromercurial could be isolated. When the holding time was increased to 240 min. the dilution with dilute sodium chloride produced an 8% yield of methoxychloromercurial. Addition of alkali to the aqueous filtrate gave an immediate heavy precipitate of yellow mercuric oxide.

1-Hydroxy-2-acetoxymercuricyclohexane

A. From the 1-Acetoxy-2-acetoxymercuricyclohexane

To 2 gm. (0.005 mole) of freshly prepared 1-acetoxy-2-acetoxymercuricyclohexane was added 2 ml. of methanol and 15 ml. of 1% aqueous potassium hydroxide. During the next 15 min. a yellow precipitate (mercuric oxide) formed gradually while an additional 5 ml. of alkali solution was added to maintain pH 9. After 15 min. longer the suspension was filtered and the filtrate, chilled to 0°C., was carefully acidified to pH 4–5 with 10% aqueous acetic acid. The solution was extracted thrice with 10 ml. portions of chloroform. The combined extracts were evaporated *in vacuo* to a volume of 5 ml. which was diluted with 10 ml. of petroleum ether (b.p. 60–70°C.). The crude 1-hydroxy-2-acetoxymercuricyclohexane weighed 0.45 gm. (25% yield) m.p. 105–107°C. This was crystallized from chloroform – petroleum ether as before to yield 0.35 gm., m.p. 113.1–113.6°C. Calc. for $C_8H_{14}O_3Hg$: C, 26.8; H, 3.90; Hg, 56.0; CH_3CO, 12.0%. Found: C, 26.9; H, 3.80; Hg, 55.7; CH_3CO, 11.8%.

B. From dd,ll (trans) 1-Methoxy-2-acetoxymercuricyclohexane

A solution of 0.1 gm. (0.00027 mole) of 1-methoxy-2-acetoxymercuricyclohexane (14) in 5 ml. of water was heated for one hour (under reflux to avoid loss of cyclohexene, detectable by odor) at 50°C. and the solvent was then distilled off under 30 mm. pressure. The distillate contained methanol. The solid residue (0.06 gm., 65 mole %) melted at 108–110°C. and its identity as 1-hydroxy-2-acetoxymercuricyclohexane was authenticated by mixed melting point. When the reaction temperature was 100°C. the yield was 90–95% of theoretical. Under similar reaction conditions 1-methoxy-2-chloromercuricyclohexane was recovered unchanged.

When *dl,ld* (*cis*) 1-methoxy-2-acetoxymercuricyclohexane was heated with water under the same conditions it was recovered unchanged after four hours, even when 2% alkali was added. Under pressure at 150°C. the aqueous solution yielded the unchanged compound after 30 min., but after 90 min. all of the mercurial had decomposed to metallic mercury.

A further example of the inertness of the *dl,ld* (*cis*) compound is demonstrated by its stability in acid. When 0.1 gm. (0.00027 mole) is dissolved in 5 ml. water and 2 ml. of 70% nitric acid is added, titration for mercury gave only one-half the theoretical amount. This would indicate that the C–Hg linkage was unbroken, even under these severe conditions, which have been

found to break down mercurials of the *dl,ld* (*trans*) configuration completely in a matter of one or two minutes. Over a period of three days however the compound slowly broke down and thiocyanate titration for mercury gave the theoretical amount.

C. From Cyclohexene

To a solution of 8 gm. (0.025 mole) of recrystallized mercuric acetate in 50 ml. of water containing 0.2 cc. conc. nitric acid was added 2.5 ml. (0.025 mole) of cyclohexene. The heterogeneous system was stirred for 20 min., after which mercuric oxide could not be precipitated by alkali from a test portion. After 40 min. more the homogeneous solution was thrice extracted with 10 ml. portions of chloroform. The combined extracts, vacuum evaporated, yielded 3.4 gm. (76% yield) of 1-hydroxy-2-acetoxymercuricyclohexane, m.p. 110.5–111°C. after crystallization from chloroform – petroleum ether and acetone. A mixed melting point with product from A and B was not lowered. The reaction can be carried out homogeneously in 1:1 water–acetone to give a yield of 85% of theoretical.

1-Hydroxy-2-chloromercuricyclohexane

A. From 1-Acetoxy-2-acetoxymercuricyclohexane

This preparation is exactly like that of the hydroxyacetoxymercurial except that hydrochloric acid rather than acetic acid was used for the neutralization. The yield was 20 mole %.

B. From 1-Acetoxy-2-chloromercuricyclohexane

When 1.1 gm. (0.0029 mole) of 1-acetoxy-2-chloromercuricyclohexane was mixed with 10 ml. of 1% aqueous alkali a yellow precipitate formed slowly over one hour during which time 10 ml. more of 1% alkali was added to maintain pH 9. After filtration and cooling the solution was acidified to pH 5 with 12% hydrochloric acid. The white precipitate (0.39 gm., 34 mole %) melted at 152.7–153.5°C. It was crystallized from 4 ml. acetone to melt at 153–153.6°C. According to mixed melting point it was identical with that produced by method A.

C. From Cyclohexene

A procedure otherwise identical with that for the acetate salt was altered by treating the reaction mixture with sodium chloride instead of extracting it with chloroform. The yield of 1-hydroxy-2-chloromercuricyclohexane was 4.0 gm. or 95% of theoretical. The product melted at 151–152°C. after crystallization from chloroform and from acetone and was not lowered by admixture with product from A and B.

Conductivity of Methanolic Mercuric Acetate Solutions

Solutions of 5 gm. of mercuric acetate (purified by crystallization from acetic acid and vacuum-dried at 50°C. for 48 hr.) dissolved in pure methanol (4) to

100 ml. volume were thermostatted at 22°C. in U tubes of 15 mm. diameter containing 20 ml. of solution. Gold plated platinum electrodes (area, 13.6 cm.^{2}) were separated by about 15 cm. in the two legs. When a d-c. potential of 62 volts was applied across this cell the current flow was 0.1 ma. as compared with 0.07 ma. for pure methanol. Addition of 0.5 ml. boron trifluoride or pyridine raised the current flow in the solution to 4–6 ma.

Catalyst Inhibition

Polymerization of cyclohexene may be initiated by addition of 0.01 mole equivalent of boron trifluoride etherate. The mixture becomes red brown and a viscous brown oil separates. This polymerization can be inhibited entirely by prior addition of 0.01 mole equivalent of pyridine; white crystalline pyridine – boron trifluoride complex settles out. When acetonitrile is used instead of pyridine, polymerization occurs, but at a much slower rate than in its absence.

Kinetic Study of Oxymercuration

The analytical procedure was that reported previously (7) except that a 5 ml. aliquot was removed for analysis and was drowned in 15 ml. of water. Addition of 1 ml. conc. hydrochloric acid sharpened the end point considerably. Both the methoxymercuration and ethoxymercuration were carried out at approximately 10^{-3} molar concentration. The cyclohexene, methanol, and ethanol were peroxide-free according to tests with titanous chloride or potassium iodide. The mercuric acetate was purified by crystallization from dilute acetic acid and was vacuum-dried. It was completely soluble in methanol. Since 0.1 ml. of cyclohexene is not completely soluble in 500 ml. of conductivity water it was not possible to effect a rate study of hydroxymercuration in this medium.

Competitive Oxymercuration with Water and Alcohols

A capillary melting point – composition diagram was constructed using the first appearance of melt and disappearance of the last crystal as limits of melting point range of mixtures of hydroxymercurial and methoxymercurial.

% methoxymercurial	0	10	31	47	58	70	72	87	100
°C., appearance of liquid	150	128	105	100	98	101	102	105	116
°C., disappearance of solid	150	145	134	120	107	109	110	113	116

The competitive reaction was carried out by addition to a solution comprising 10 gm. (0.0314 mole) of mercuric acetate in 90 ml. methanol and 100 ml. of water of 3.5 ml. (0.035 mole) of cyclohexene in 10 ml. methanol. Aliquots were withdrawn and added to aqueous sodium chloride. The solution was filtered and the filtrate extracted with three 10 ml. portions of chloroform.

The melting points were determined for the precipitate and evaporated extract. The reaction mixture was heterogeneous for about four minutes when the reaction was complete in about 15 min. The per cent of methoxymercurial was 61%. A slight alteration in the procedure involving a lesser amount of diluent aqueous sodium chloride showed negligible chloroform extract, and in this case the percentage of methoxymercurial in the product was 85% at the beginning and 70% at the end of the experiment. A further alteration involving the use of 150 ml. of methanol and 50 ml. of water gave a reaction mixture which was homogeneous after 30 sec. The product comprised 90% methoxymercurial and 10% hydroxymercurial. Comparable studies with water–ethanol mixtures show that the hydroxymercurial predominates in the product.

1-Ethoxy-2-chloromercuricyclohexane

When 1.6 ml. (0.016 mole) of cyclohexene in 100 ml. absolute ethanol was treated with 5.1 gm. (0.0157 mole) of mercuric acetate, this salt was entirely consumed after seven hours. Treatment of this solution after 18 hr. with aqueous sodium chloride yielded 5.7 gm. (88%) of 1-ethoxy-2-chloromercuricyclohexane, m.p. 56–57°C. Two crystallizations from boiling ethanol (20 ml. per gm.) raised this melting point to 61–61.5°C. Calc. for $C_8H_{13}OHgCl$: C, 26.5; H, 4.15%. Found: C, 26.8; H, 4.26%.

1-tert-Butoxy-2-chloromercuricyclohexane

A suspension of 12.72 gm. (0.04 mole) of mercuric acetate in 100 ml. of *tert*-butyl alcohol (distilled from sodium) was treated with 1 ml. of boron trifluoride etherate and 4 ml. (0.04 mole) of dry cyclohexene. After three hours the agitated mixture became homogeneous. It was filtered into 250 ml. of water to which 40 ml. of saturated aqueous sodium chloride was then added to cause precipitation. After 12 hr. the aqueous phase was decanted from the viscous oil (9.7 gm.), which was then evacuated under reduced pressure. It then largely solidified after treatment with 60 ml. of ethyl ether. Filtration removed 7.71 gm., m.p. 106–112°C. (50% of theory). This was crystallized from 40 ml. boiling 95% ethanol and then from absolute ethanol, m.p. 115–116°C. Calc. for $C_{10}H_{19}OHgCl$: C, 30.7; H, 4.91%. Found: C, 30.5; H, 5.04%. When this compound is dissolved in dilute aqueous sodium hydroxide or in strong aqua ammonia and the cold solution containing sodium chloride is acidified carefully with acetic acid the mercurial is recovered unchanged. When the original *tert*-butyl alcohol was not water-free the product was contaminated with 1-hydroxy-2-chloromercuricyclohexane.

Treatment of an ethanolic solution of the chloromercurial with aqueous potassium bromide precipitated 1-*tert*-butoxy-2-bromomercuricyclohexane, m.p. 95.5–96° after crystallization from ethanol. Calc. for $C_{10}H_{19}OHgBr$: C, 27.6; H, 4.40%. Found: C, 27.7; H, 4.47%.

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A 40°C. ISOTHERMAL CALORIMETER[1]

By E. J. Caule[2] and C. C. Coffin

Abstract

A 40° Bunsen-type isothermal calorimeter has been built and tested. The working substance, benzalacetone, is thermostatted by the vapor of methylal boiling under a constant pressure. An impurity in the benzalacetone makes it necessary to calibrate the instrument in exactly the same way in which it is to be used. Under carefully controlled conditions and with a constant mantle thickness the reproducibility is of the order of 0.2%. With about half the benzalacetone in the solid state, the calorimeter constant was found to be 0.0455 (± 0.0001) gm. of mercury per calorie. This instrument, which can be readily adapted to micro and semimicro work, was designed primarily for the direct determination of the heats and rates of certain enzymatic and bacteriological processes.

Introduction

A preceding paper (2) describes a Bunsen-type isothermal calorimeter in which heat is determined from the volume change of a mass of solid and liquid naphthalene at its melting point 80°C. and thermostatted with the vapor of benzene boiling under a constant predetermined pressure. The present paper describes the construction, operation, and calibration of a similar instrument operating at 40°C. Here the calorimetric substance is benzalacetone and methylal is the thermostatting vapor. This combination was selected with the idea of developing an isothermal calorimeter operating in the optimum temperature range of certain enzymatic and bacteriological processes, thus enabling their heats and rates to be directly determined. It was made much smaller than the naphthalene instrument in order to further test the applicability of this type of calorimeter to micro and semimicro measurements. The following paper (1) describes the determination of the heat of the explosive crystallization of amorphous ("explosive") antimony in this apparatus.

Experimental

The Calorimeter

Apart from the fact that the benzalacetone calorimeter is considerably smaller than the naphthalene calorimeter (working volumes are 15 and 120 cc. respectively) the two are so similar in the details of construction and operation that it is unnecessary to repeat their description here. As before, the volume change is determined from the movement of mercury in a calibrated capillary tube which in this case consisted of 3 m. of selected pyrex capillary twice doubled back on itself to give three 1 m. lengths lying horizontally side by side on a 1 m. mirror glass scale graduated in millimeters. One average centimeter of

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this tube corresponded to 0.664 cal., so that up to 200 cal. per run could be measured. The capillary was calibrated over its entire length with pellets of mercury. With methylal as the thermostatting vapor, zero drift was obtained with the barostat operated at about 3 cm. of mercury below normal atmospheric pressure. Like the larger calorimeter this apparatus may be left running indefinitely without attention if the bent-down far end of the measuring capillary is immersed in mercury.

The Benzalacetone

A substance must fulfil certain requirements to be suitable as a filling for a solid–liquid phase change calorimeter. It must be available in quantity and be so stable at its melting point to light, air, moisture, etc., that it may be obtained in a state of great purity by repeated crystallization. Not only must it be capable of purification to such a degree that there is no appreciable increase of melting point with the fraction melted (i.e., it must exhibit no "premelting") but it must remain so when kept indefinitely at its melting point in the presence of mercury. Finally, its melting point must of course correspond to the temperature at which it is desired to operate the calorimeter.

As already stated, one of the main objects of this work was to develop an isothermal calorimeter suitable for the direct determination of the heats of bacteriological and enzymatic processes, many of which have their optimum temperatures in the neighborhood of 40°C., where they proceed at a measurably slow rate. An obviously possible working substance was phenol (melting point 40°C.) which has indeed been used (3) in standard Bunsen calorimeters thermostatted in water-baths. Several attempts, however, to use phenol in these vapor-jacketed calorimeters have indicated that it is too unstable and difficult to purify. Even after it was in the apparatus and so protected from air and moisture the color continued to deepen and the melting point to fall, presumably on account of the action of light or mercury.

Of the few available compounds melting at about 40°C., benzalacetone seemed most likely to fulfil the requirements outlined above, and an attempt was accordingly made to obtain about 500 gm. of the highest purity. Three kilograms of Eastman's best benzalacetone was distilled in nitrogen at a low pressure and a large middle fraction was subjected to many systematic fractional crystallizations. The final almost water-white product was again distilled in a low pressure of nitrogen, and a small middle fraction taken for filling the calorimeter and dilatometers for solid and liquid density measurements.

It was found with even the most colorless specimens that the last portion to solidify was always reddish in color and froze at a temperature distinctly below that at which crystallization had begun. Moreover, the total amount of the low-melting dark red fraction continually increased as further recrystallizations were carried out. This behaviour indicates that an impurity is continually being formed, presumably by oxidation at the double bond, and

that it is impossible to purify benzalacetone completely by recrystallization in the presence of air. The fact that the benzalacetone in the calorimeter (and protected from air) has shown no change in color or melting point after many months in the molten condition bears out the view that the dark red low-melting fraction is an oxidation product.

Several determinations of the volume change on melting were made with purified samples of benzalacetone, which gives exceptionally large and well formed crystals. In these experiments the volume of mercury entering or leaving the dilatometers between equilibria at two different temperatures was determined by weighing. A temperature range of about 10°C. on either side of the melting point was covered. All measurements gave the densities of liquid and solid at the melting point (40.02°C.) to be 1.134 and 1.015 respectively. The volume change on melting is accordingly 0.104 cc. per gm. Premelting necessitated a short extrapolation to obtain the density of the solid at the melting point.

Although the benzalacetone filling does not deteriorate after it is in the calorimeter it contains enough impurity to lower the melting point as the solid/liquid ratio increases. This of course seriously interferes with the precision and general usefulness of the calorimeter, as both the calorimeter constant and the operating temperature become dependent on the thickness of the solid mantle. Although handicapped in this way, the calorimeter has features that render it useful in many cases of the type for which it was designed, and benzalacetone is being used as the 40°C. filling until a more satisfactory substance is obtained.*

Calibration of the Calorimeter

The calorimeter was calibrated by dissipating a measured quantity of electrical energy in a coil of resistance wire wound on a glass rod frame, insulated with "Formvar" varnish and immersed directly in the mercury-filled well on which a solid mantle of the desired thickness had been formed. Current and potential leads were taken out through a 4 cm. plug of cotton wool. After the drift had been made small (by adjusting the pressure on the boiling methylal) and had remained constant for several five minute periods the run was started by switching the current from a "dummy" to the heating coil and starting the stopwatch. The rate of heat input was usually rather slow in order to simulate the conditions of a reaction proceeding at a measurable rate and to facilitate correcting for the fact that owing to the impurity of the benzalacetone the drift changed as the mantle melted.

When heat is liberated in the calorimeter, benzalacetone is melted, the concentration of impurity in the liquid is diminished, and the temperature of solid–liquid equilibrium rises. Thus if an exothermic run is started with the inner and outer temperatures the same (i.e., zero drift) it will finish with the

**The authors would be grateful for suggestions regarding a more suitable compound for this purpose.*

inner temperature higher than the outer so that heat losses will exceed heat gains and the drift will be negative, i.e., in the direction of smaller volume. In the case of slow runs where the system is never very far from equilibrium the actual drift will not be far from the mean of the initial and final drifts, so that in making a series of such runs in which the approximate heat change is known it has been found convenient to set the methylal temperature at a value that will make the final drift equal and opposite to the initial drift. When the reaction being measured is so rapid that the total heat change may be regarded as taking place at the beginning of the run, only the final drift need be taken into consideration in estimating heat gains or losses.

The impurity in the benzalacetone affects the behavior of the calorimeter not only by lowering the melting point but also, through the phenomenon of "premelting", by making the calorimeter constant dependent to some extent on the solid/liquid ratio. The heavier the mantle employed in a run, the smaller the value of the "constant". For a complete calibration it is thus necessary to make runs at different mantle thicknesses and construct an empirical curve from which a normalizing factor may be obtained and a "constant" applicable to any mantle thickness calculated.

The ratio of solid to liquid may be determined at the beginning of any run from the total volume of mercury in the calorimeter or, more conveniently, from the methylal temperature (Beckman thermometer in vapor) corresponding to zero drift. For mantles that are not too thick it was found experimentally that a 0.1 degree rise in this methylal temperature resulted in a 0.15% increase in the calorimeter constant.

Results

Instead of attempting to obtain a complete calibration curve over a wide range of solid/liquid ratios the reproducibility of the instrument was tested at an approximately constant mantle thickness. This was a fairly heavy mantle for this type of calorimeter as about half the benzalacetone was solid at the beginning of each run. A sequence of such runs (selected as previously described (2)) was taken from the data of each of two operators working with different electrical setups, heating coils, etc., and using varying amounts and rates of power input. A period of about eight months during which the calorimeter was in continuous use elapsed between the two series.

In a total of 25 such calibration runs no trend of calorimeter constant (grams mercury per calorie) with any significant variable can be observed. To indicate the precision of the instrument in these runs it is thus sufficient to state the mean value of the calorimeter constant together with the average deviation from this mean, viz., 0.0455 ($\pm$ 0.0001). In all these runs the methylal temperature at zero drift fell between 39.9° and 40.0°C.

Division of this calorimeter constant by the volume change on melting stated above (0.104 cc. per gm.) gives 30.8 cal. per gm. or 4500 cal. per mole for the latent heat of fusion of benzalacetone.

This calorimeter has given some promising results on the rates and heats of the coagulation of milk casein by rennin and the hydrolyses of urea by urease in buffered solutions. Further studies of such systems are, however, being deferred until a substance more satisfactory than benzalacetone has been obtained.

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STUDIES ON EXPLOSIVE ANTIMONY

IV. THE HEAT OF EXPLOSION AT 40°C.[1]

By C. C. Coffin and C. E. Hubley[2]

Abstract

The heat of the "explosive" crystallization of electrolytically deposited amorphous antimony has been directly determined at 40°C. in a modified Bunsen-type calorimeter using benzalacetone as the working substance. Correction was made for the amount of antimony trichloride in the deposits and for the crystallization that had taken place between their preparation and explosion. Sixteen runs on exceptionally uniform specimens containing between 4.0 and 7.9% antimony trichloride gave 21.8 cal. per gm. for the heat of explosion, which thus appears to be independent of the antimony trichloride content.

Introduction

Under certain conditions of concentration, temperature, and current density, antimony may be deposited electrolytically from antimony trichloride–hydrochloric acid solutions in an amorphous form which on heating, scratching, or mechanical shock undergoes a more or less explosive crystallization (5). This deposit appears to be the only example of a metal which can be obtained in any quantity in the vitreous or supercooled condition, and it has been studied to some extent in this laboratory from this point of view (2, 3, 5). The present paper deals with a determination of the heat of explosion in the previously described 40° isothermal calorimeter (1).

These unstable antimony deposits contain from 2 to 12% of antimony trichloride (7) (depending chiefly on the concentration of the electrolyzed solution) which is partially volatilized during the explosion. The sensitivity of the deposits to heat or shock and the speed and violence of the crystallization are greatly dependent on the amount of antimony trichloride present (3). Thus the crystallization of deposits from concentrated solutions (50–80% antimony trichloride) takes place very sluggishly, and at room temperature is difficult to initiate by shock alone. On the other hand, specimens prepared from dilute solutions (<4% antimony trichloride) explode violently at the slightest touch, and may be prepared only in small quantities and at low temperatures.

The main object of the present work was to see if the total heat of explosion was also dependent upon the amount of antimony trichloride in the deposit. This point cannot be decided from the earlier data of Cohen and Strengers (8), who found the heat of transition of different specimens to vary between 19.2 and 23.8 cal. per gm. It was also desired to investigate the suitability of the isothermal calorimeter for this type of semimicro measurement.

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Experimental

Preparation of Specimens for Heat Measurements

Cylindrical cathodes of the explosive metal were deposited in pairs on $\frac{1}{16}$ in. brass rods from antimony trichloride (in 10% hydrochloric acid) solutions at room temperature in a manner previously described (2). In this arrangement the cathodes themselves served as stirrers. They were revolved in a 10 cm. diameter circle about a central anode at 300 r.p.m. and in every turn around the anode each cathode rotated five times about its own axis. Very homogeneous and uniform deposits may be obtained in this way. The current density was kept roughly constant (0.1 amp. per cm.^{2}) by manually increasing the current as the cathodes grew. At the lower concentrations, cathodes were occasionally lost by explosion in the cell before attaining a sufficiently large size. Others were accidentally exploded before getting them placed in the calorimeter. Finally however 16 specimens weighing from 2 to 6 gm. were successfully exploded in the calorimeter. Pertinent details about the specimens are given in columns 1 to 4 of Table I.

TABLE I

Specimen number	Per cent $SbCl_3$ in solution	Weight of cathode, gm.	Per cent $SbCl_3$ in cathode	Weight of amorphous Sb present at explosion, gm.	Heat of transition, cal./gm. Sb
1	22.6	3.321	5.8	3.05	22.5
2	22.6	4.291	5.8	3.94	21.8
3	22.6	4.747	5.8	4.34	21.6
4	20.4	3.959	5.6	3.65	21.2
5	20.7	5.619	5.6	5.18	21.3
6	20.7	3.798	5.6	3.54	21.2
7	21.2	4.404	5.7	4.05	21.2
8	50.0	2.734	7.9	2.44	22.0
9	50.0	1.959	7.9	1.75	20.8
10	49.9	3.002	7.9	2.69	23.6
11	12.6	3.612	4.8	3.34	21.3
12	12.9	3.767	4.8	3.53	21.6
13	12.9	6.173	4.8	5.74	22.2
14	13.5	5.198	4.9	4.84	22.8
15	13.5	4.254	4.9	3.94	22.2
16	9.5	2.924	4.0	2.75	22.2

Determination of the Heat of Explosion

It has been shown in a previous paper (3) that these unstable antimony deposits undergo a nonexplosive first order crystallization at a rate given by the equation

$$2.303 \log k = 31.4 - \frac{27300}{RT}.$$

To minimize thermal crystallization the specimens were therefore kept at 0°C. until they could be placed in the calorimeter. Corrections were made for the amount crystallized during preparation, storage, and pre-explosion time in the calorimeter.

The weighed specimens for the heat measurements were carefully transferred to close fitting test tubes stoppered by a cork carrying a long glass tube. With the test tube and specimen completely immersed in mercury in the calorimeter well, this glass tube extended through the cotton plug in the calorimeter opening and was used to explode the specimen when the drift had become constant. By pressing down and turning the tube the sharp edges of its open lower end could be made to scratch and explode the specimen. The mercury in the measuring capillary started to move within a second or two after the explosion, which could usually be felt as a "bump" through the long tube. The run was continued until the drift had again become constant for several five minute periods. In runs of this kind where all the heat is liberated at once the final drift was assumed to apply throughout the run. After removal from the calorimeter the exploded deposit was stripped off the brass cathode, placed in a long narrow test tube, and melted to distill all occluded antimony trichloride into the upper part of the tube. When cold the antimony trichloride was dissolved in hydrochloric acid solution and determined volumetrically.

The actual weight of amorphous antimony at the instant of explosion is the total weight of the deposit less the weight of antimony trichloride and corrected as explained above for the crystallization that had taken place during storage. These values are given in column 5 of Table I. In column 6 are listed the heats of transition. These were calculated from the mercury displacement corrected for drift and capillary irregularities (4). The evaluation of the calorimeter constant (0.0455 gm. of mercury per cal.) has already been described (1).

Discussion of Results

The heats of explosion of specimens deposited from solutions of similar concentration are averaged in Table II.

It is evident from the table that, within the concentration range investigated and the limits of error of the measurements, the concentration of antimony

TABLE II

HEATS OF EXPLOSION AT 40°C. OF DEPOSITS CONTAINING DIFFERENT AMOUNTS OF ANTIMONY TRICHLORIDE

Specimen number	% $SbCl_3$ in solution	% $SbCl_3$ in deposit	Heat of explosion, cal./gm.
16	9.5	4.0	22.2
11, 12, 13, 14, 15	13.1	4.8	22.0
4, 5, 6, 7	21.0	5.6	21.2
1, 2, 3	22.6	5.8	21.8
8, 9, 10	50.0	7.9	22.1
		Average heat of explosion at 40°C.	21.8

trichloride in amorphous antimony has no effect on its heat of crystallization, which appears to be a true physical constant of the material. Although the present results at 40°C. are not strictly comparable with those of Cohen and Strengers (8) at 18°C. the two sets of data agree reasonably well. The earlier results were not corrected for thermal crystallization before explosion and the deposits were probably not as homogeneous as those used in the present work. Photographs of deposits in Cohen's papers show a rough botryoidal structure and in some cases are definitely those of a mixed deposit, i.e., partly crystalline and partly amorphous. In the present work all mixed deposits were discarded. Specimen No. 16, for example, was the only one of six cathodes made under identical conditions that was free from "warts" of light grey crystalline antimony. It should be noted that these conditions correspond to the borderline between crystalline and noncrystalline deposition determined by Cohen and Coffin (6). This is probably the reason why our mean value is slightly higher than that of Cohen and Strengers. It does not seem possible to carry out heat measurements over a greater range of antimony trichloride content than that covered in the present work. Deposits containing more than about 8% antimony trichloride are too difficult to explode in the calorimeter and those containing less than 4% are too unstable to handle and prepare in sufficient quantity.

Although the work described here throws no direct light on the chemical nature of the "occluded" antimony trichloride or on the physical mechanism of its retention, it does indicate that the compound does not affect the intrinsic properties of the amorphous metal. Like the rate and activation energy of the slow thermal crystallization (3) the heat of explosion is independent of the antimony trichloride, which thus appears to act merely as a diluent. This behavior is not inconsistent with the marked stabilizing effect of occluded antimony trichloride and its suppression of thermal and electrical conductivity (3). The compound does not seem to be present as antimony trichloride however. Preliminary experiments have shown that it cannot be extracted by solvents from the powdered material (ground in a mortar without explosion under liquid nitrogen), and X-ray diffraction photographs of deposits rich in antimony trichloride have shown nothing but the diffuse rings characteristic of the supercooled metal. The extraction experiments are being repeated and extended with radioactive antimony as a tracer.

In spite of the fact that the benzalacetone contains an impurity the 40° isothermal calorimeter has proved to be a very satisfactory instrument for this type of semimicro heat measurements.

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APPLICATION DE LA REACTION DE MEERWEIN A L'ACIDE β-METHYLCINNAMIQUE ET AU METHACRYLATE DE METHYLE[1]

PAR PHILIBERT L'ECUYER ET CHARLES-A. OLIVIER[2]

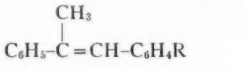
Sommaire

L'acide β-méthylcinnamique se comporte de la même façon que l'acide cinnamique en présence des sels de diazonium aromatiques substitués. Il a donné les dérivés du méthylstilbène suivants: le méthylstilbène, les 4-,3- et 2-nitro-β-méthylstilbènes, le 4-chloro-β-méthylstilbène, le 4-bromo-β-méthylstilbène, le 4-méthoxy-β-méthylstilbène, le 4, β-diméthylstilbène et le 4-phényl-β-méthylstilbène. D'autre part le méthacrylate de méthyle avec divers sels de diazonium a donné naissance aux dérivés de l'α-chloro-α-méthylhydrocinnamate de méthyle suivants: les 4-,3- et 2-nitro-α-chloro-α-méthylhydrocinnamates de méthyle, le 4, α-dichloro-α-méthyl-hydrocinnamate de méthyle, le 4-bromo-α-chloro-α-méthylhydrocinnamate de méthyle, le 4-méthoxy-α-chloro-α-méthyl-hydrocinnamate de méthyle et le 4, α-diméthyl-α-chlorohydrocinnamate de méthyle. L'hydrolyse du 4-nitro-α-chloro-α-méthylhydrocinnamate de méthyle dans des conditions différentes a fourni l'acide 4-nitro-α-méthylcinnamique et l'acide 4-nitro-α-chloro-α-méthylhydrocinnamique. Enfin le sel de diazonium de la *p*-nitraniline et la benzalacétophénone ont donné le 4-nitro-α-benzoylstilbène.

Introduction

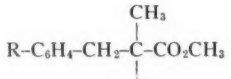
La réaction de Meerwein entre les sels de diazonium aromatiques substitués et les composés carbonyles possédant une double liaison entre les atomes de carbone α et β se passe de deux façons. Si le reste alkyle sur le carbone β est saturé, le groupement phényle introduit par l'intermédiaire du sel de diazonium s'unit au carbone α (1, 2, 3, 4, 8, 9, 10, 11, 13). Si, d'autre part, le carbone β est porteur d'un substituant saturé, le groupement phényle s'attaque au carbone β et il y a alors addition de chlore sur le carbone α (1, 7, 8, 9).

Comme l'acide cinnamique donne avec les sels de diazonium des dérivés du stilbène, on pouvait s'attendre à ce que l'acide β-méthylcinnamique fournisse des dérivés du méthylstilbène avec un bon rendement en raison de l'effet inductif du groupement méthyle dans ce dernier. Nous avons effectivement synthétisé les dérivés du méthylstilbène (I) suivants: le méthylstilbène, les 4-, 3- et 2-nitro-β-méthylstilbènes, le 4-chloro-β-méthylstilbène, le 4-bromo-β-méthylstilbène, le 4-méthoxy-β-méthylstilbène, le 4, β-diméthylstilbène et le 4-phényl-β-méthylstilbène. Les rendements sont meilleurs que pour la synthèse des stilbènes correspondants.



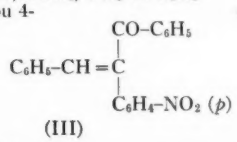
(I)

R = H, NO_2, Cl, Br, OCH_3, CH_3 ou C_6H_5 en position 2-,3- ou 4-



(II)

R = NO_2, Cl, Br, OCH_3 ou CH_3 en position 2-,3- ou 4-



(III)

[1] *Manuscrit reçu le 14 juin 1950.*
Contribution du Département de Chimie de l'Université Laval, Québec, Qué.
[2] *Boursier du Conseil National des Recherches.*

Certains dérivés du méthylstilbène peuvent être obtenus par la méthode de Grignard. C'est ainsi que le méthylstilbène et le 4-méthoxy-β-méthylstilbène avaient été préparés respectivement par Klages (6) et Lévy et ses collaborateurs (12), mais la méthode de Meerwein est plus générale, parce qu'elle permet d'introduire dans la molécule un substituant halogéné ou nitré. Ayant vérifié que la présence d'un groupement méthyle sur le carbone β favorise l'introduction d'un groupement phényle en α, nous avons songé que, dans le même ordre d'idée, en employant comme réactif un composé non-saturé possédant un substituant saturé sur chacun des deux atomes de carbone reliés par la double liaison, on devrait obtenir de meilleurs rendements que lorsque l'atome de carbone α est simplement porteur d'un atome d'hydrogène. Comme, en plus, le produit obtenu devrait posséder une fonction acide ou du moins un groupement facilement hydrolysable, nous avons cru que la réaction de Meerwein pourrait constituer une méthode de synthèse des acides cinnamiques substitués en α et même des acides correspondants saturés et chlorés en position α. Voilà pourquoi nous avons appliqué la réaction de Meerwein au méthacrylate de méthyle.

Avec divers sels de diazonium aromatiques substitués, le méthacrylate de méthyle a donné des dérivés de l'α-chloro-α-méthylhydrocinnamate de méthyle (II): les 4-, 3- et 2-nitro-α-chloro-α-méthylhydrocinnamates de méthyle, le 4, α-dichloro-α-méthylhydrocinnamate de méthyle, le 4-bromo-α-chloro-α, méthylhydrocinnamate de méthyle, le 4-méthoxy-α-chloro-α-méthylhydrocinnamate de méthyle et le 4, α-diméthyl-α-chlorohydrocinnamate de méthyle.

L'hydrolyse à l'acide chlorhydrique à point d'ébullition constant du 4-nitro-α-chloro-α-méthylhydrocinnamate de méthyle a donné l'acide 4-nitro-α-méthylcinnamique. D'autre part, l'hydrolyse du même ester à l'aide d'un mélange d'acide acétique et d'acide chlorhydrique a donné naissance à l'acide 4-nitro-α-chloro-α-méthylhydrocinnamique.

Dans une publication antérieure (9), nous avons rapporté que les sels de diazonium réagissent avec la benzalacétone. Une réaction analogue est aussi possible avec la benzalacétophénone; c'est ainsi que la condensation du sel de diazonium de la *p*-nitraniline avec la benzalacétophénone a donné le 4-nitro-α-benzoylstilbène (III). Le rendement est cependant moins élevé dans ce dernier cas. De plus, l'isolation du produit de la réaction est plus difficile; car, avant de l'obtenir, il faut d'abord distiller l'excès de benzalacétophénone dont le point d'ébullition est élevé.

Partie expérimentale

L'amine mise en solution dans l'acide chlorhydrique à 25% (50 ml. pour 0.1 mole) est refroidie à 0°C. dans un bain de sel et de glace et diazotée par l'addition lente d'une solution de nitrite de sodium dans l'eau (8.4 g. pour 0.1 mole). Le sel de diazonium ainsi préparé est alors ajouté à une suspension d'une quantité équimoléculaire du composé carbonyle dans un volume d'acétone suffisant pour le maintenir en solution (environ 50 ml. pour 0.1 mole), d'acétate de sodium et de chlorure cuivrique dihydraté (respectivement 22 g.

et 4.2 g. pour 0.1 mole). Au début de la réaction ou du moins pendant l'addition de la solution diazotée il faut garder le mélange à la température la plus basse qui permette un dégagement gazeux et maintenir une vigoureuse agitation mécanique. Celle-ci doit être continuée pendant le temps que dure le dégagement gazeux soit environ deux à trois heures. Si la réaction débute à basse température, on permet alors au mélange de prendre la température du laboratoire.

Le mélange est ensuite soumis à la distillation à la vapeur d'eau pour éliminer l'acétone et les substances secondaires volatiles, et on rend le résidu alcalin par addition d'ammoniaque. Refroidi, le produit de la réaction se présente généralement sous la forme d'une masse résineuse (rarement solide). On décante le liquide surnageant et on lave plusieurs fois à l'ammoniaque diluée et à l'eau pour enlever les dernières traces de cuivre. Si le résidu est gommeux, on le dissout dans le chloroforme ou l'éther, on sèche la solution sur du sulfate de sodium anhydre, on évapore le solvant et on distille dans le vide (0.02 mm.). Si, au contraire, le résidu est solide, on peut le triturer à l'acide acétique glacial ou le sublimer dans le vide.

Les diverses condensations que nous avons effectuées sont indiquées dans le Tableau I et à moins d'indication contraire les composés obtenus ont été cristallisés de l'alcool éthylique.

TABLEAU I

CONSTANTES PHYSIQUES ET RÉSULTATS D'ANALYSE DES COMPOSÉS SYNTHÉTISÉS

Réactifs		Fract. de mole	Produit de la réaction	P.é., °C. 0.02 mm.	P.f., °C.	Rend., %	Analyses	
Comp. carbonyle	Amine						Calculé	Trouvé
Acide β-méthyl-cinnamique	Aniline	0.05	I H	85–90	81–82 (6)	36	C = 92.8 H = 7.2	C = 92.0 H = 7.3
"	*p*-Nitraniline	"	I 4-NO_2	90–100(sub.)	107–108	32	C = 75.63 H = 5.46	C = 75.4 H = 5.6
"	*m*-Nitraniline	"	I 3-NO_2	145–150	....	28	C = 75.63 H = 5.46	C = 74.7 H = 5.5
"	*o*-Nitraniline	"	I 2-NO_2	105–115	72–73	18	C = 75.63 H = 5.46	C = 75.3 H = 5.7
"	*p*-Chloraniline	"	I 4-Cl	60–65 (sub.)	86.5–87.5	35	Cl = 15.54	Cl = 15.7
"	*p*-Bromaniline	"	I 4-Br	60–70 (sub.)	87–89	23	Br = 29.32	Br = 29.6
"	*p*-Anisidine	"	I 4-OCH_3	110–120	83–84 (12)	11	C = 85.7 H = 7.14	C = 85.1 H = 7.4
"	*p*-Toluidine	"	I 4-CH_3	90–100	55–56	11	C = 92.69 H = 7.31	C = 91.9 H = 7.5
"	*p*-Aminodiphényle	"	I 4-C_6H_5*	115–120(sub.)	141.5–142.5	21	C = 93.33 H = 6.67	C = 92.3 H = 6.6
Méthacrylate de méthyle	*p*-Nitraniline	0.2	II 4-NO_2	....	102–103	67	C = 51.27 H = 4.66 Cl = 13.78	C = 51.4 H = 5.0 Cl = 13.6
"	*m*-Nitraniline	0.5	II 3-NO_2	130–135	38.5–39.5	63	Cl = 13.78	Cl = 13.3
"	*o*-Nitraniline	"	II 2-NO_2	115–120	....	27	Cl = 13.78	Cl = 11.0
"	*p*-Chloraniline	0.1	II 4-Cl	90–95	....	37	Cl = 28.74	Cl = 28.8
"	*p*-Bromaniline	0.2	II 4-Br	105–110	....	32	Hal = 38.1	Hal = 37.7
"	*p*-Anisidine	0.5	II 4-OCH_3	100–105	....	26	Cl = 14.64	Cl = 11.8
"	*p*-Toluidine	"	II 4-CH_3	105–110	....	57	Cl = 15.67	Cl = 15.5
Benzalacétophénone	*p*-Nitraniline	0.1	III*	210–215	188–189	20	C = 76.06 H = 4.55	C = 75.9 H = 4.8

**Cristallisé de l'acide acétique glacial.*

Acide 4-nitro-α-méthylcinnamique

Le 4-nitro-α-chloro-α-méthylhydrocinnamate de méthyle (8 g.), à l'ébullition pendant 15 h. dans 150 ml. d'acide chlorhydrique 20%, a donné avec un rende-

ment à peu près quantitatif l'acide 4-nitro-α-méthylcinnamique. Cet acide cristallise de l'alcool éthylique en fines aiguilles jaunâtres de p.f. 205–207°C. (5). Calculé pour $C_{10}H_9O_4N$: C, 57.96; H, 4.35%. Trouvé: C, 57.5; H, 4.7%.

Acide 4-nitro-α-chloro-α-méthylhydrocinnamique

Le 4-nitro-α-chloro-α-méthylhydrocinnamate de méthyle (84 g.), en solution dans 500 ml. d'acide acétique glacial et 300 ml. d'acide chlorhydrique concentré, est maintenu à l'ébullition pendant 21 h. La solution est ensuite versée dans 2 litres d'eau et le produit se solidifie. L'acide 4-nitro-α-chloro-α-méthylhydrocinnamique est soluble dans l'alcool éthylique, l'alcool méthylique, l'acide acétique et l'acétate de méthyle. Il cristallise sous forme de petits prismes blancs du chloroforme et fond à 140–142°C. Rendement quantitatif. Calculé pour $C_{10}H_{10}O_4N$ Cl: Cl, 14.58%. Trouvé: Cl, 14.7%.

Remerciements

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PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL XXXVI. LINEAR POLYESTERS OF 2,3-BUTANEDIOL[1]

By R. W. Watson, N. H. Grace, and J. L. Barnwell

Abstract

New polyesters with basic units containing 6, 7, 8, 9, 10, 13, and 14 chain atoms have been prepared from *levo*-2,3-butanediol and ethyl oxalate, ethyl malonate, dimethyl terephthalate, maleic anhydride, succinic, glutaric, adipic, azelaic, and sebacic acids, and from *meso*-2,3-butanediol and *o*-phthalic anhydride. Esterification of 2,3-butanediol with a dibasic acid, or its anhydride, is accompanied by a side reaction, in which butanone-2 and the cyclic methyl ethyl ketal are formed. The purified polyesters, with the exception of the poly-malonate, appear to be composed of regularly recurring acid and diol segments over the molecular weight ranges investigated. Without exception they are amorphous resins or balsams. Polyesters formed from saturated aliphatic dibasic acids become progressively softer as the number of methylene groups in the acid segment increases. The polymeric oxalate, on distillation *in vacuo*, is converted to a macrocrystalline cyclic monomer.

Under specified conditions, the condensation of a dihydric alcohol with a dicarboxylic acid forms a polymeric ester, unless the number of chain atoms in the basic unit is less than seven (3). Esters of the type $-(-CO-(CH_2)_x-CO-O-(CH_2)_y-O-)-$ are usually microcrystalline solids (4), although in a few instances side reactions interfere with the regular development of the chains. Poly-ethylene malonate is amorphous (4), and the condensation of hexanediol with dimethyl sebacate results in the formation of an insoluble gel (12). A cross-linked structure also develops on heating 1,3-butanediyl *o*-phthalate under pressure (1). In the present communication, the preparation and properties of a series of previously undescribed 1,2-dimethylethylene polyesters are reported.

Elementary analyses of polyesters prepared by conventional methods (2, 4, 5) are listed in Table I, along with the corresponding number average molecular

TABLE I

Esters of 2,3-butanediol

Ester	Basic unit formula	Base mole	Chain atoms in unit	Molecular weight	End groups present	Analysis calculated on	Carbon and hydrogen, %	
							Calc.	Found
1. Poly-oxalate	$C_6H_8O_4$	144	6	450*	Carbethoxyl Hydroxyl	$C_{20}H_{30}O_{13}$	C– 50.21 H– 6.28	C– 50.08 50.36 H– 6.19 6.26
2. Poly-malonate	$C_7H_{10}O_4$	158	7	1060*	Carbethoxyl Hydroxyl	$C_{44}H_{66}O_{25}$	C– 53.11 H– 6.64	C– 55.65 55.95 H– 6.64 6.94

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TABLE I—*Continued*

Ester	Basic unit formula	Base mole	Chain atoms in unit	Molecular weight	End groups present	Analysis calculated on	Carbon and hydrogen, %	
							Calc.	Found
3. Poly-succinate	$C_8H_{12}O_4$	172	8	1610†	Carboxyl	$C_{76}H_{114}O_{40}$	C– 54.74 H– 6.84	C– 54.53 55.03 H– 6.90 7.12
4. Poly-glutarate	$C_9H_{14}O_4$	186	9	1630†	Carboxyl	$C_{77}H_{120}O_{36}$	C– 57.05 H– 7.41	C– 56.85 57.14 H– 7.45 7.49
5. Poly-adipate	$C_{10}H_{16}O_4$	200	10	1170†	Carboxyl	$C_{56}H_{90}O_{24}$	C– 58.64 H– 7.85	C– 58.26 58.13 H– 8.06 8.01
6. Poly-azelate	$C_{13}H_{22}O_4$	242	13	2570†	Carboxyl	$C_{139}H_{236}O_{44}$	C– 63.96 H– 9.05	C– 63.46 64.04 H– 8.99 9.14
7. Poly-sebacate	$C_{14}H_{24}O_4$	256	14	2070†	Carboxyl	$C_{108}H_{186}O_{32}$	C– 65.00 H– 9.33	C– 65.55 64.92 H– 9.62 9.54
8. Poly-maleate	$C_8H_{10}O_4$	170	8			$C_{96}H_{122}O_{49}$	C– 55.98 H– 5.93	C– 55.69 55.80 H– 6.60 6.65
9. Poly-*o*-phthalate	$C_{12}H_{12}O_4$	220	8	1990‡	Hydroxyl Carboxyl	$C_{108}H_{110}O_{37}$	C– 64.86 H– 5.50	C– 64.88 64.91 H– 5.78 5.86
10. Poly-*meso* *o*-phthalate‖	$C_{12}H_{12}O_4$	220	8	1200†	Carboxyl	$C_{68}H_{66}O_{24}$	C– 64.45 H– 5.21	C– 64.18 H– 5.51
11. Poly-*p*-phthalate	$C_{12}H_{12}O_4$	220	10	1550†	Carboxyl	$C_{80}H_{78}O_{28}$	C– 64.60 H– 5.25	C– 64.22 64.12 H– 5.56 5.59
12. Cyclic oxalate	$C_6H_8O_4$	144		145§		$C_6H_8O_4$	C– 50.00 H– 5.55	C– 50.06 50.46 H– 5.72 5.85

*—*Ebullioscopic.*
†—*End-group.*
‡—*Viscosimetric.*
§—*Rast.*
‖—*Prepared from meso-diol; all others from the levo-isomer.*

weights, determined ebullioscopically (9), viscosimetrically (18), or by end-group titration. With the exception of the poly-malonate, the percentages of carbon and hydrogen obtained by analysis are close to the values calculated for chains of known number average molecular weight with known end-groups. This evidence supports the view that the dimethyl-substituted polyesters, like the ethylene polyesters (4), are composed of linear chains of known structure over the molecular weight ranges investigated. Moreover, the results are in accord with those previously presented for poly-*levo*-2,3-butanediyl *o*-phthalate (18) which revealed agreement between end-group and ebullioscopic molecular weights, and a linear viscosity – molecular weight relation from $\overline{M}_n$ 480 to 2400. The side reaction, which accompanies direct esterification and leads to the formation of butanone-2 and 2,4,5-trimethyl-2-ethyl-1,3-dioxacyclopentane (11, 18), therefore does not interfere with the regular development of the chains.

All these polyesters are amorphous resins or balsams, a fact that conforms with the view that molecular symmetry is the dominant factor in micro-crystallinity. If resins prepared from a series of saturated aliphatic dicarboxylic acids are compared, it is apparent that they become increasingly more mobile as the number of methylene groups in the acid segment increases. As a result of greater irregularity in the structure of the macromolecule the dimethyl-substituted resins display a wider range of solubilities (see experimental section) than do the corresponding ethylene polyesters (4, 17).

The hardness of poly-1,2-dimethylethylene *o*-phthalate presents a rather striking anomaly (16, 17). The greater geometrical bulkiness and increased asymmetry of the 1,2-dimethyl substituted chains, compared with those of poly-ethylene phthalate, might be expected to occasion a decrease in hardness. The hypothesis that attractive forces residing in the ester groups shorten the glycol units to the *cis*-form (13) is applied to 2,3-butanediyl *o*-phthalate in Fig. 1. Barriers to rotation about the central C–C bond have been established in the *racemic* and *meso*-2-3-dibromobutanes (14), and they may be assumed to occur in the 2,3-butanediols. Evidence for relatively unrestricted rotation at the bonds about the ester linkages has also been reported (7, 8). Three loci of relatively free rotation remain in each half of an arbitrary unit segment, i.e., two about the ester linkage, and one at the CO–C bond (marked *a*, *b*, *c*,

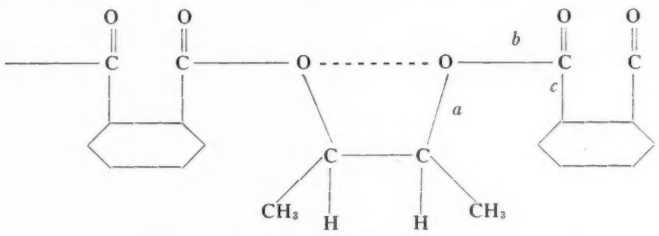

FIG. 1. *Hypothetical unit segment of poly-1,2-dimethylethylene phthalate.*

respectively in Fig. 1). The *mer* is therefore composed of two relatively stiff units: the benzene nucleus, and the two-carbon butanediol chain, each connected by three flexible linkages. This concept indicates a relatively inflexible chain, with which the greater hardness and higher flow point of the dimethyl-substituted polyester are associated.

Experimental

Levo-2,3-butanediol, obtained from the fermentation of wheat by *Bacillus polymyxa* (10, 19) was redistilled to $n_D^{25} = 1.4310$, $[\alpha]_D^{25} = -13.0$. The mixed *meso-*, *dextro-*, and *levo*-diols (15) produced by *Aerobacter aerogenes* were fractionated through a Stedman column to boiling point 182.4°C., $n_D^{35} = 1.4327$, $[\alpha]_D^{25} = +0.07$. Since isomerization takes place under the conditions for polyesterification (18), further purification of the *meso*-diol was unnecessary.

Succinic acid (Eastman 237), recrystallized from dilute nitric acid, had m.p. 185°C.; maleic anhydride, distilled from xylene, had m.p. 50°–53°C.; *o*-phthalic anhydride (Eastman 331), purified by sublimation *in vacuo*, had m.p. 130°–131°C.; dimethyl terephthalate, prepared from terephthalic acid and methanol in the presence of sulphuric acid, had m.p. 142°–143°C. after purification by sublimation at 85°C. (1 mm.); adipic acid (Eastman 1029), recrystallized from 50% ethanol, had m.p. 151°–153.5°C. Eastman ethyl oxalate, ethyl malonate, ethyl adipate, glutaric, azelaic, and sebacic acids were used without further purification.

Short-chain polyesters were prepared by previously described methods (2, 4, 5). Acidic esters, used in end-group molecular weight determinations, were prepared and purified as described in a previous paper (18).

1. Poly-levo-2,3-butanediyl Oxalate

Equimolar quantities of *levo*-2,3-butanediol (180 gm.) and ethyl oxalate (292 gm.) were heated with 0.50 gm. magnesium chloride hexahydrate at atmospheric pressure in a Claisen flask fitted with condenser and receiver. The reaction became vigorous at about 160°C. After 23 hr. at 160° to 206°C. the yield of distillate was 181.3 gm. or 98.6% of theoretical, calculated as ethanol. Besides ethanol the distillate contained small amounts of diol and ethyl oxalate. The resinous reaction product was dissolved in an equal volume of ether, washed rapidly with water to remove catalyst, and dried. Vacuum fractionation of the polymer at 60° to 170°C. (0.2 mm.) yielded eight fractions and a polymeric residue. A macrocrystalline cyclic monomer separated from fractions 4 to 8 on standing. Recrystallized from anhydrous ethanol, and resublimed *in vacuo* at 78°C., the monomer had a melting range of 99.6° to 101.5°C. (corr.). This melting range was unchanged by three subsequent vacuum sublimations. Presumably the crystals represent stereoisomeric mixtures. The Rast molecular weight was 145 (observed values: 144, 146; theoretical: 144). Calc. for $C_6H_8O_4$: C, 50.00; H, 5.55. Found: C, 50.06, 50.46; H, 5.72, 5.85. A more detailed report on the cyclic *meso-* and *levo*-oxalates will be presented in a subsequent paper.

The polymeric residue was a light brown balsam which became semisolid at room temperature. Dried to constant weight *in vacuo* at 78°C., its apparent molecular weight (ebullioscopic) was 450. Calc. for $C_{20}H_{30}O_{13}$: C, 50.21; H, 6.28%. Found: C, 50.08, 50.36; H, 6.19, 6.26%.

2. Poly-levo-2,3-butanediyl Malonate

The poly-malonate was prepared from equimolar quantities of ethyl malonate (160 gm.) and *levo*-diol (90 gm.) by the method outlined for the oxalate. After addition to the reactants of 0.15 gm. magnesium chloride hexahydrate and 0.20 gm. of sodium metal, alcohol distilled over fairly rapidly at 170°C. After 11 hr. at 170° to 220°C., the resin was cooled, taken up in ether, washed, dried over Drierite, and the ether removed (100°C. (1 mm.)).

The purified polyester was a viscous reddish brown balsam, soluble in benzene, acetone, chloroform, ethanol, and diethyl ether; it was insoluble in petroleum ether and in water. Dried to constant weight at 78°C. (0.03 mm.), its apparent molecular weight (ebullioscopic) was 1050 (observed values: 1050, 1060). Calc. for $C_{44}H_{66}O_{25}$: C, 53.11; H, 6.64. Found: C, 55.65, 55.95; H, 6.64, 6.94. This anomalous elementary analysis prompted complete re-preparation from the original reactants, and repurification. Analysis showed that the percentages of carbon and hydrogen were unchanged in the second preparation (found: C, 55.51; H, 6.65). The structure of this polyester is therefore probably more complex than that of other members of the series.

3. Poly-levo-2,3-butanediyl Succinate

Levo-2,3-butanediol (1.2 moles) and succinic acid (1 mole) were reacted together under nitrogen at 150° to 180°C. for five hours at atmospheric pressure. The reaction was continued *in vacuo* for an additional period of 13 hr. at 200° to 220°C. (1 to 3 mm.). Samples were removed after 4, 7, 8, 10, 14 and 18 hr., washed, and dried to constant weight *in vacuo* at 100°C. All samples were pale transparent resins, the final sample having an apparent molecular weight in boiling chloroform of 3750 (by isothermal distillation (6), $\bar{M}_n$ = 3150). This polyester was tough, nonsticky, deformable by the fingers, and slightly elastic; soluble in benzene, toluene, acetone, methyl acetate, chloroform, acetic acid, methanol, ethanol, and dioxane; insoluble in carbon disulphide, isopropyl ether, petroleum ether, and water. A less highly polymerized sample, after carboxylation, purification, and drying to constant weight, had an end-group molecular weight of 1610 (observed values: 1580, 1600, 1640). Calc. for $C_{76}H_{114}O_{40}$: C, 54.74; H, 6.84%. Found: C, 54.53, 55.03; H, 6.90, 7.12%.

4. Poly-levo-2,3-butanediyl Glutarate

Equimolar quantities of glutaric acid (13.2 gm.) and *levo*-2,3 butanediol (9 gm.) were directly esterified at 139° ± 1°C. for 43 hr., and subsequently for 46 hr. at 170° to 190°C. under deoxygenated nitrogen. Excess glutaric acid (7.2 gm.) was then added, and the reaction continued at 190°C. for three

hours. The product was washed in boiling water (five changes, 75 ml.), dissolved in benzene, dried, and the solvent removed *in vacuo*. The purified polyester was a light brown, viscous balsam; soluble in benzene, acetone, chloroform, methanol, ethanol, and diethyl ether; insoluble in carbon tetrachloride, petroleum ether, and water. Dried to constant weight it had an end-group molecular weight of 1600 (observed values: 1560, 1630). Calc. for $C_{77}H_{120}O_{36}$: C, 57.05; H, 7.41. Found: C, 56.85, 57.14; H, 7.45, 7.49.

5. Poly-levo-2,3-butanediyl Adipate

The poly-adipate was prepared both by direct esterification and by ester interchange from ethyl adipate. The products had the same general properties. During direct esterification with equimolar quantities of *levo*-diol and adipic acid, 77% of the amount of water which would be expected for complete polyesterification distilled during the period under atmospheric pressure. The purified polyester was a thick yellowish syrup; soluble in benzene, toluene, acetone, ethyl acetate, butyl acetate, chloroform, carbon tetrachloride, methanol, ethyl ether, and dioxane; insoluble in carbon disulphide, isopropyl ether, petroleum ether, and water. After carboxylation and subsequent repurification it had an end-group molecular weight of 1170 (observed values: 1160, 1180). Calc. for $C_{56}H_{90}O_{24}$: C, 58.64; H, 7.85%. Found: C, 58.13, 58.26; H, 8.01, 8.06%.

6. Poly-levo-2,3-butanediyl Azelate

Levo-2,3-butanediol (22.5 gm.) and azelaic acid (47.0 gm.) were reacted together at 140°C. for 16 hr., and 180°C. for 120 hr. under carbon dioxide. Approximately one half of the reaction mixture was then removed, 10 gm. of azelaic acid added, and the reaction continued at 180°C. for three hours. After washing and drying to constant weight the acidic resin had an end-group molecular weight of 2570 (observed values; 2560, 2570). It was a moderately thick yellowish syrup; soluble in benzene, acetone, ethyl acetate, chloroform, methanol, ethanol, and ethyl ether; slightly soluble in petroleum ether; and insoluble in water. Calc. for $C_{139}H_{236}O_{44}$: C, 63.96; H, 9.05%. Found: C, 64.04, 63.46; H, 9.14, 8.99%.

7. Poly-levo-2,3-butanediyl Sebacate

One mole of *levo*-diol (90 gm.) and 0.5 mole of sebacic acid (101 gm.) were heated together at 180° to 200°C. under deoxygenated nitrogen at atmospheric pressure for six hours. The distillate comprised 77% of the theoretical water for complete polyesterification. Heating was continued at 200° to 210°C. (1 mm.) for six hours, during which time the excess glycol distilled off. The crude resin had an acid value of 0.8. After washing, drying, and further purification by molecular distillation, it was a clear yellow syrup with an end-group molecular weight of 2070; soluble in benzene, toluene, acetone, butyl acetate, chloroform, carbon tetrachloride, methanol, ethyl ether, isopropyl

ether, and dioxane; insoluble in petroleum ether and in water. Calc. for $C_{108}H_{186}O_{32}$: C, 65.00; H, 9.33%. Found: C, 64.92, 65.55; H, 9.62, 9.54%.

8. Poly-levo-2,3-butanediyl Maleate

Maleic anhydride (94.5 gm.) and *levo*-2,3-butanediol (175 gm.) were heated together under nitrogen at 180° to 210°C. until most of the water had escaped. The excess glycol was then removed by vacuum distillation at 210° to 215°C. The resin, a clear reddish brown balsam, was purified by prolonged molecular distillation. Rapid hydrolysis of this polyester in 0.1 *N* alkali made it impossible to obtain an acid value. It was soluble in benzene, toluene, acetone, butyl acetate, chloroform, ethyl ether, and dioxane; insoluble in carbon disulphide, petroleum ether, isopropyl ether, and water. After 10 hr. *in vacuo* at 200°C. the solubilities were unchanged. After 26 hr. *in vacuo* it had become insoluble in acetone. Calc. for an assumed molecular weight of 2000: $C_{96}H_{122}O_{49}$: C, 55.98; H, 5.93%. Found (after 10 hr. *in vacuo* at 200°C.): C, 55.69, 55.89; H, 6.60, 6.65%. Found (after 26 hr. *in vacuo* at 200°C.): C, 55.72; H, 6.64%.

9. Poly-levo-2,3-butanediyl o-Phthalate

The preparation and properties of this polyester were described in a previous paper (16). A purified sample from equimolar quantities of reactants had a viscosimetric molecular weight of 1990. Calc. for $C_{108}H_{110}O_{37}$: C, 64.86; H, 5.50%. Found: C, 64.88, 64.91; H, 5.78, 5.86%.

If care is taken to exclude oxygen during preparation, the poly-phthalate is a pale straw colored solid. In acetone solution at 0°C. it is rapidly decolorized (10 min.) by oxygen containing 1 to 3 mole % of ozone. After solvent removal under nitrogen, a clear colorless solid remains. The ozone treatment causes no detectable change in molecular weight.

10. Poly-meso-2,3-butanediyl o-Phthalate

This polyester was prepared from *meso*-2,3-butanediol by the method described for the acidic *levo*-phthalates. It resembled the *levo*-phthalate in physical properties, except that it was somewhat softer at the same degree of polymerization. Its end-group molecular weight was 1200 (observed values: 1190, 1210). Calc. for $C_{68}H_{66}O_{24}$: C, 64.45; H, 5.21%. Found: C, 64.18; H, 5.51%.

11. Poly-levo-2,3-butanediyl Terephthalate

Anhydrous *levo*-diol (25 gm.) and dimethyl terephthalate (25 gm.) were heated with 0.15 gm. of sodium metal at 139 ± 1°C. for 24 hr. under nitrogen. The reaction product after acidification and purification had an end-group molecular weight of 1550. In boiling chloroform its average molecular weight was 1430 (observed values: 1390, 1460). It was a clear amorphous glass. Calc. for $C_{80}H_{78}O_{28}$: C, 64.60; H, 5.25%. Found: C, 64.12, 64.22; H, 5.59, 5.56%.

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NOTES

Note on the Stereoisomers of 2,3-Butanediol Produced by Yeast*

It has been known for some time that yeast produces a small amount of 2,3-butanediol during the normal alcoholic fermentation of glucose. Over 60 years ago French workers isolated a butanediol from solutions fermented by yeast (1, 3, 4). They believed it to be isobutanediol, but the properties reported agree closely with those of 2,3-butanediol, which is now known to be formed by yeast. Unfortunately no measurement of its optical rotation was made and, as far as the author knows, no one else has isolated a large enough sample to attempt this. However, it has been shown that diacetyl (8) and *dl*-acetoin (7), if added to a fermenting yeast solution, are reduced to give *levo*-rotatory 2,3-butanediols with rotations of $-2.4°$ and $-5.5°$ respectively. Since these rotations are considerably lower than that of pure D- (*levo*)-2,3-butanediol (5) some of the *meso* or *dextro*-rotatory isomers must be produced as well.

An investigation has been made in order to find out which isomers of 2,3-butanediol are produced by yeast during the normal alcoholic fermentation of glucose. A solution (750 ml.) containing glucose (18%) and yeast extract (0.5%) was fermented anaerobically by a strain of distiller's yeast. It was then cleared by zinc hydroxide precipitation, concentrated to two-thirds of its volume to remove most of the alcohol, and extracted with ether in a continuous extractor. The ether extract contained a considerable amount of water, so it was extracted again in a smaller extractor. The 2,3-butanediol was finally obtained in a pale yellow aqueous solution (8 ml.) which was found to contain 86.4 mgm. of the diol, by measurement of the acetaldehyde formed on periodate oxidation. The diol was then separated from glycerol and other interfering substances by partition chromatography on a Celite column, using the technique described elsewhere (6) but working with 6 ml. of the aqueous solution (64.8 mgm. of diol) and using 30 gm. of Celite in a column of 36 mm. diameter. The chromatogram was developed with ethyl acetate, and eight 100 ml. fractions collected. Most of the 2,3-butanediol (54 mgm.) was found in the third and fourth fractions. These were combined and concentrated to 10 ml. Water was removed by azeotropic distillation with benzene (23 ml.), then pyridine (4.5 ml.) and *p*-nitrobenzoyl chloride (250 mgm.) were added, and the benzene distilled out, as previously described (9). The crude ester was purified by washing its solution, in chloroform, with sodium carbonate (6%). After evaporation of the chloroform a crystalline residue was obtained, (109 mgm.), on treating with aqueous acetone. When dissolved

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in chloroform (4 ml.) it was observed to have an optical rotation of $-1.90°$ (2 dm.). This corresponds to a specific rotation of $-34.9°$ which is about 67% of that of the pure D- (*levo*)-2,3-butanediol di-*p*-nitrobenzoate. Recrystallization from acetone gave some pure *meso*-2,3-butanediol di-*p*-nitrobenzoate as well as crystals of the *levo*-rotatory isomer, both of which were identified by mixed melting points with authentic samples (9).

It can be concluded from this that the 2,3-butanediol produced by yeast is a mixture of the *levo*-rotatory and *meso* isomers containing at least 67% of the former. The presence of a small amount of the racemic form is not excluded. The specific rotation of 2,3-butanediol normally produced by yeast should then be approximately $-8.5°$ to $-8.7°$ which is higher than the rotation of the diol formed on reduction of *dl*-acetoin by yeast. This would be expected even if 2,3-butanediol is formed naturally by reduction of acetoin since the acetoin formed from pyruvate by yeast is known to be *levo*-rotatory (2).

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